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FRACTIONATION AND CONVERSION OF LIGNINS FROM STEAM-TREATED FORESTRY RESIDUES TO HIGHER VALUE PRODUCTS

PREPARED FOR:

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PREFACE

This work was performed by Forintek Canada Corp. under contract to the Department of Supply and Services (DSS Contract No. 048SZ.23216-8-9037) during the period from January, 1989 to June, 1991.

The research provides information on the fractionation of steam-treated aspenwood lignins and their conversion to methyl aryl ethers, fuels and phenolic compounds. As well, an assessment of lignin fractions and produced phenolic fractions as adhesives for the panel products industry is provided.

The work is consistent with the general objectives of the Efficiency and Alternative Energy Technology Branch, which includes the goal to make better use of biomass as a source of fuels and chemicals. The intended audience for this report includes government representatives, other contractors in the field, representatives of the biomass industry in Canada, and the scientific community in general.

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EXECUTIVE SUMMARY

Bioconversion systems are technically feasible but high capital and operating costs relative to oil and gas technologies necessitate research and development to reduce the costs and risks. Steam pretreatment has been shown to be the most economical means of rendering wood susceptible to enzymatic hydrolysis to sugars, which can then be converted to liquid fuels and chemicals. To maximize the cost effectiveness of conversion of biomass to liquid fuels it is essential to utilize the lignin component of any woody feedstock. The objectives of this project were: to fractionate by ultrafiltration lignins extracted from steam-treated aspenwood; to study conversion of the isolated lignins to methyl aryl ethers, fuels and phenolic compounds; and to assess their application as adhesives for panel products.

The alkaline extracts of steam-treated aspenwood water-insolubles were subjected to ultrafiltration. The yields of fractions isolated from constant volume and multiple batch ultrafiltrations of the alkaline extracts are similar but not comparable with the original single batch ultrafiltration experiments. Lignin-fractions isolated from single batch, multiple-batch, and constant volume ultrafiltrations were characterized. Batch ultrafiltration gives polydisperse fractions and a substantial low molecular weight component may be present in the highest average molecular weight fractions. Preparation of an alkaline solution from ethyl acetate-extracted lignin highlighted one of the problems with the lignin recovery method used. The method, which includes heating of the acidified lignin extract, leads to the production of alkali-insoluble material. The molecular weight distributions and properties of the lignins recovered after ultrafiltration are affected by the recovery process. The characteristics of the fractions obtained by ultrafiltration suggest that it may be inappropriate to fractionate this type of lignin into more than two or three fractions.

Studies using electrochemical methods to convert the lignins to low molecular weight chemicals were made. The acid precipitable lignins produced by anodic oxidation in basic aqueous media undergo changes involving a decrease in phenyl groups, an increase of the carboxylic groups of the lignins, and an opening of benzylic rings.

Characterization of the acetone-solubles recovered after electrolysis indicate drastic changes from the starting lignin. These changes are indicative of the formation of carbonyl carbons in esters or quinoidal structures, but the former interpretation is favored.

The yields of low molecular weight products produced by oxidation with increasing passage of charge indicate that the first formed products are undergoing further reaction.

Attempts to provide a parametric analysis of the electrolysis process were unsuccessful. However, the experiments indicated little production of volatile organic products and limited carbon dioxide production. Analysis of ethyl acetate solubles produced indicated the production of alkanedioic acids. Problems experienced with the analysis of the alkaline electrolysis solutions is an example of the difficulties encountered in analyzing lignin reaction products, and the need for analytical methods development.

Products of oxidation of steam-treated aspenwood lignin using peroxydisulfate, ($S_2O_8^{2-}$-Cu^{II}), in acetic acid are dependent on the available functional groups within the lignin, and can either lead to substantial depolymerization when the available hydroxyl functions are blocked and polymerization when they are available. Only low yields of monomeric products were obtained.

Metalloporphyrin oxidations on lignin were not investigated because of concerns with the observation of trace quantities of chlorinated products, the observation in two cases of oxidation in the absence of metal complex, and that when oxidation occurred only very low conversions were observed and products were dependent on starting material.

Preliminary assessments were made of some of the lignin-fractions obtained to date by the formulation of lignin-phenol-formaldehyde (lignin-PF) resins and production of small particleboards. The low molecular weight lignin fractions from batch and constant volume ultrafiltration are more reactive for the formulation of lignin-phenolic adhesives than the corresponding higher molecular weight lignin-fractions. The unfractionated aspenwood lignin could be used to replace 10-20 % of a core PF waferboard adhesive and 30-40 % of a face PF waferboard adhesive.

Preparation of a powder, pre-cure resistant surface adhesive for waferboard demonstrated that steam-treated lignin could be used to replace 30% by solid weight of a phenol-formaldehyde in the formulation. The lignin-PF resin had a curing speed similar to a commercial surface phenolic resin.

Through a sub-contract with Concordia University it was demonstrated that the steam-treated lignins could be successfully utilized in polyblend formulations with an epoxy (EP) adhesive (Ciba Geigy AY 103-HY 956). When compared with the EP control, the adhesive strength in shear of the EP-20% unfractionated lignin and EP-20% <10K lignin fraction disclosed superior performance, i.e., 15% and 30% higher respectively. The adhesive shear strength of the EP-<10K lignin fraction polyblends at a lignin content superior than 10%, after accelerated weathering is still higher than the EP control. In the same polyblends kraft lignin has little effect on shear strength. In the polyurethane (Desmodur E14-Desmophen 1920D)-lignin sealant systems, the effect of lignin upon the mechanical properties is less obvious than in the EP-L blends.

Computer modelling of the process for the fractionation and recovery of lignin estimated the cost of fractionation of lignin using ultrafiltration followed by acid precipitation to be 17.5 cents/kg. This is 62% higher than the cost of lignin recovered by acid precipitation alone, which is estimated at 12 cents/kg.

An economic analysis of lignin use in wood products adhesives and as fuel octane enhancers was undertaken and led to the following four conclusions.

There are significant deficiencies in the knowledge base on the availability and value of the aspen/poplar timber resource from which lignin would be obtained. To rectify these deficiencies, the following issues should be addressed: the cost and available supply of the resource; and, the relative values that can be generated from the resource through various uses such as manufacturing pulp, paper, and solid wood products, as well as from fuels and adhesives.

Much of the research into developing lignin as a substitute for phenol in adhesive resins and as a base substance from which fuel additives can be refined is based on using lignin that results as a co-product from a biomass liquefaction process. One of the processes that generates lignin is pulping. Traditionally, lignin derived from pulping has been used as an important and integral component in the energy cycle of pulp mills. Its potential diversion to other uses raises a number of questions about the impact on energy demand patterns in that industry. Little is known of these potential impacts and further analysis is required.

The potential for lignin as a substitute for phenol in PF resins is of little benefit or interest if these resins become obsolete as a result of more stringent regulatory standards with regard to formaldehyde emissions. While this analysis has identified some of the key aspects of policy and regulation development on this issue, more detailed evaluation is required as a basis for guiding future research efforts on the potential for lignin in the development of new adhesives.

The most important market characteristic with respect to evaluating the potential for alkyl aryl ethers, is the need for them to contribute to lower vehicle fuel and exhaust emissions when blended into motor fuels. Research focussed primarily or solely on achieving cost-competitiveness for alkyl aryl ethers relative to petrochemical-based ethers will likely result in a failure of the aryl ethers to gain any market position simply because they fail to address the primary needs of the market. The direction of the lignin research should therefore shift towards meeting the environmental imperatives of the fuels market, specifically emissions reduction and performance and driveability.

From the work undertaken the following recommendations are made for future research.

The significant deficiences in the knowledge base on the availability and value of the aspen/poplar timber resource from which lignin would be obtained must be addressed. The cost and available supply of the resource and the relative values that can be generated from the resource through alternative uses must be determined.

If the above analysis determines that continued research on this feedstock is worthwhile and warranted, then the following research on the production of low molecular weight chemicals by oxidation of lignin should be considered.

Electrochemical oxidation should be investigated using flow cells, using as feedstock acid precipitated lignin and the lignin containing alkaline extracts of steam-treated aspenwood. Peroxydisulfate, ($S_2O_8^{2-}$-Cu^{II}), oxidation of steam-treated aspenwood lignin and the acetylated and methylated derivatives should be examined under alkaline conditions. Water-soluble hemins merit attention and should be evaluated on available types of lignin in both aqueous and organic systems.

If any of the above demonstrate potential to produce increased yields of precursors for aryl methyl ethers then future research must take into account that the most important market characteristic with respect to evaluating the potential for alkyl aryl ethers, is the need for them to contribute to lower vehicle fuel and exhaust emissions when blended into motor fuels. The direction of the lignin research should therefore then shift towards meeting the environmental imperatives of the fuels market, specifically emissions reduction and performance and driveability. This latter directive is equally applicable to research directed at aryl methyl ethers regardless of the feedstock or conversion route.

More detailed evaluation of the policy and regulatory environments with respect to formaldehyde emissions is required as a basis for guiding future research efforts on the potential for lignin in the development of new adhesives. If this evaluation indicates that further development of lignin-PF adhesives is worthy of merit, then, the adhesives results for the powder, pre-cure resistant surface adhesive for waferboard should be demonstrated at pilot plant scale by the preparation of the powder adhesive on a sufficient scale to allow the manufacture of full size panels.

For the epoxy-lignin polyblends demonstrated to be technically feasible, an economic assessment of their production is warranted to determine if they are economically viable.

RÉSUMÉ À L'INTENTION DE LA DIRECTION

Techniquement, la production d'essence par bioconversion est faisable, mais les investissements nécessaires et les coûts d'exploitation sont élevés par rapport à la technique de transformation du pétrole; il sera donc nécessaire de procéder à des recherches et du développement pour réduire ces coûts ainsi que les risques encourus. Un prétraitement à la vapeur s'est avéré la méthode la plus économique permettant de rendre le bois sensible à l'hydrolyse enzymatique en sucres, qu'il est ensuite possible de transformer en carburants liquides et en d'autres substances chimiques. Pour rentabiliser au maximum la conversion de la biomasse en carburants liquides, il est essentiel d'utiliser la fraction lignine de toute charge ligneuse. Cette étude avait deux objectifs : fractionner par ultrafiltration les lignines extraites du bois de tremble traité à la vapeur; convertir les lignines isolées en éthers méthyliques d'aryles, en carburants et en substances phénoliques; finalement, évaluer leur application comme adhésifs dans la fabrication de panneaux.

Les extraits alcalins des résidus insolubles dans l'eau obtenus par traitement du bois de tremble à la vapeur furent soumis à une ultrafiltration. Le traitement à volume constant ou en lots multiples donne des rendements analogues, mais qui ne sont pas comparables à ceux obtenus lors des premières expériences

d'ultrafiltration en lots simples. On a caractérisé les fractions lignines isolées par ultrafiltration en lots simples, en lots multiples et à volume constant. L'ultrafiltration en lots donne des fractions polydispersées et il se peut qu'une portion substantielle de composantes à masse moléculaire faible se retrouve dans les fractions dont la masse moléculaire moyenne est élevée. La préparation d'une solution alcaline de lignine extraite à l'acétate d'éthyle a mis en évidence un des problèmes posés par la méthode de récupération utilisée. Par cette méthode, qui inclut le chauffage de l'extrait de lignine acidifié, des matières insolubles en milieu basique sont produites. La distribution de la masse moléculaire ainsi que les propriétés des lignines récupérées par ultrafiltration sont affectées par le procédé de récupération. Les caractéristiques des fractions obtenues par ultrafiltration semblent indiquer qu'il peut ne pas être souhaitable de fractionner ce genre de lignine en plus de deux ou trois fractions.

Des études furent réalisées sur la transformation de la lignine par des méthodes électrochimiques en composés chimiques de masse moléculaire faible. Les lignines précipitables en milieu acide produites par oxydation anodique en milieu aqueux basique subissent des modifications faisant intervenir une diminution des groupements phényles, une augmentation des groupements carboxyliques des lignines ainsi qu'une ouverture des noyaux benzyliques.

La caractérisation des composés solubles dans l'acétone récupérés après électrolyse indique des modifications remarquables de la lignine de départ. Ces modifications indiquent qu'il y a formation de carbonyles sous forme soit d'esters, soit de structures quinoïdes, mais c'est la première hypothèse qui est favorisée.

Les rendements en produits de masse moléculaire faible obtenus par oxydation avec augmentation de la charge passante montrent que les premiers produits formés subissent d'autres réactions.

Les tentatives de faire une analyse paramétrique du procédé d'électrolyse n'ont pas eu de succès. Toutefois, les expériences ont montré que la production de composés organiques volatils était faible et celle de dioxyde de carbone, limitée. L'analyse des substances produites solubles dans l'acétate d'éthyle indique la production d'acides alcanedioïques. Les problèmes suscités par l'analyse des solutions d'électrolyse alcaline sont un exemple des difficultés rencontrées lors de l'analyse des produits de réaction de la lignine; ils signalent donc la nécessité de mettre au point des méthodes d'analyse.

L'oxydation de la lignine de bois de tremble traité à la vapeur au moyen de peroxydisulfate ($S_2O_8^{2-}$-Cu^{II}) dans l'acide acétique donne des produits différents selon les groupements fonctionnels présents dans la lignine; ils peuvent soit entraîner une dépolymérisation importante lorsque les groupements hydroxyles sont bloqués, soit une polymérisation lorsqu'ils sont libres. Les rendements en monomères ont toujours été faibles.

L'oxydation des métalloporphyrines de la lignine n'a pas été étudiée étant donné les craintes suscitées par l'observation de traces de produits chlorés, l'observation - dans deux cas - d'une oxydation en l'absence d'un complexe métallique et le fait que, en cas d'oxydation, les taux de conversion étaient très faibles et les produits obtenus variaient selon le matériau de départ.

Des évaluations préliminaires ont été faites de certaines des fractions de lignine obtenues jusqu'ici en les utilisant dans des formulations de résines lignine-phénol-formaldéhyde (lignine-PF) et dans la production de petits panneaux de particules. Les fractions de lignine à faible masse moléculaire obtenues par ultrafiltration en lots et à volume constant sont plus efficaces pour la formulation d'adhésifs ligninophénoliques que ne le sont les fractions correspondantes à masse moléculaire plus élevée. La lignine de bois de tremble non fractionnée pourrait être utilisée pour remplacer des adhésifs de type PF à raison de 10 à 20 % dans les panneaux de copeaux à âmes et de 30-40 % dans les panneaux de copeaux contreplaqués.

La préparation d'un adhésif de surface en poudre avec agent de durcissement, assez résistant pour être utilisé dans les panneaux de copeaux, a démontré que la lignine traitée à la vapeur pouvait servir à remplacer une résine phénol-formaldéhyde dans la formulation dans une proportion de 30 % en masse solide. La vitesse de durcissement du mélange lignine-résine PF était semblable à celle d'une résine phénolique de surface vendue dans le commerce.

Une étude en sous-traitance réalisée à l'Université Concordia a démontré que les lignines traitées à la vapeur pouvaient être utilisées avec succès en mélange mécanique de polymères avec un adhésif époxydique (EP) (AY 103-HY 956 de la Ciba Geigy). En comparaison de l'adhésif EP témoin, les mélanges EP-20 % de lignine non fractionnée et EP-20 % de lignine de la fraction < 10 k offraient une meilleure résistance au cisaillement, soit 15 % et 30 % respectivement. Après vieillissement accéléré, la résistance au cisaillement des adhésifs composés d'un mélange de polymères d'EP-lignine de la fraction < 10 k et ayant une teneur en lignine supérieure à 10 % est quand même meilleure que celle de l'EP témoin. Dans les mêmes mélanges de polymères, la présence de lignine kraft a peu d'effet sur la force de cisaillement. Dans les produits de scellement à base de polyuréthane (Desmodur E14-Desmophen 1920D) et de lignine, l'effet de la lignine sur les propriétés mécaniques est moins évidente que dans les mélanges de type EP-L.

La modélisation par ordinateur des procédés de fractionnement et de récupération de la lignine a permis d'évaluer à 17,5 cents le kilogramme les coûts du fractionnement de la lignine par ultrafiltration et sa récupération par précipitation en milieu acide. Ces coûts sont supérieurs de 62 % à ceux de récupération de la lignine par précipitation en milieu acide seulement, qui est évaluée à 12 cents le kilogramme.

Une analyse économique a été entreprise de l'utilisation de la lignine comme adhésif dans les produits du bois et comme additif antidétonnant dans l'essence; cette étude a mené à quatre conclusions :

La base de connaissances sur la disponibilité et la valeur des ressources en billes de tremble/peuplier dont il serait possible d'extraire la lignine comporte des lacunes importantes. Pour combler ces lacunes, il faudrait s'attaquer aux problèmes suivants : le coût et la disponibilité des ressources; la valeur relative des produits qui peuvent être obtenus à partir de la ressource par diverses utilisations telles que la fabrication de pâtes, de papiers et de produits solides du bois ainsi que de carburants et d'adhésifs.

Une bonne partie de la recherche sur le remplacement du phénol par la lignine dans les résines adhésives et sur son utilisation comme substance de base pouvant donner par raffinage des additifs à carburant se base sur l'utilisation de la lignine obtenue comme sous-produit d'un procédé de liquéfaction de la biomasse. Un des procédés produisant de la lignine est le défibrage. Traditionnellement, la lignine produite selon ce procédé a constitué une composante importante et intégrale du cycle de l'énergie dans les usines de pâtes à papier. La possibilité de l'utiliser à d'autres fins soulève un certain nombre de questions quant aux répercussions que cette utilisation pourrait avoir sur les besoins d'énergie dans cette industrie. On sait peu de choses sur ces répercussions potentielles; d'autres analyses seront donc nécessaires.

La possibilité de se servir de lignines pour remplacer le phénol dans les résines PF a peu d'avantages ou d'intérêt si ces résines deviennent périmées par suite d'une réglementation plus strictes des émissions de formaldéhyde. Cette analyse a permis de définir certains des aspects clés de l'élaboration d'une politique et d'un règlement relatif à cette question. Toutefois, il sera nécessaire de procéder à une évaluation plus détaillée qui servira de base aux recherches entreprises à l'avenir sur le potentiel de la lignine dans le développement de nouveaux adhésifs.

L'aspect le plus important du processus d'évaluation du potentiel de mise en marché des éthers alkyliques d'aryles est la nécessité que leur mélange avec un carburant contribue à abaisser la consommation de carburant ainsi que les émissions des véhicules automobiles. Une recherche centrée principalement ou uniquement sur la rentabilité financière des éthers alkyliques d'aryles, comparativement aux éthers produits par la pétrochimie, ne permettra probablement pas aux éthers obtenus à partir du bois de gagner une partie du marché, tout simplement parce qu'elle ne répond pas aux besoins primaires du marché. La recherche sur la lignine doit donc s'orienter de façon à satisfaire aux exigences écologiques en matière de carburant, en s'attaquant de façon spécifique à la réduction des émissions, à la performance et à la facilité de conduite des véhicules.

Les travaux entrepris jusqu'ici permettent de formuler les recommandations suivantes en ce qui concerne la recherche à venir :

Il faut que soient comblées les lacunes importantes qui existent dans la base de connaissances sur la disponibilité et la valeur des ressources en billes de tremble/peuplier dont il est possible d'extraire la lignine. Il faut aussi établir les coûts et la disponibilité des ressources ainsi que la valeur relative des sommes d'argent qui peuvent être produites par d'autres utilisations des ressources.

Si ces analyses indiquent qu'il vaut la peine et qu'il est justifié de poursuivre les recherches sur ce genre d'alimentation, il sera alors temps d'envisager de faire les recherches suivantes sur la production de substances chimiques à faible masse moléculaire par oxydation de la lignine.

On devrait étudier l'oxydation électrochimique de la lignine dans des cuves à circulation continue. La charge d'alimentation devrait être de la lignine précipitée en milieu acide et des extraits alcalins contenant de la lignine obtenue par traitement de bois de tremble à la vapeur. On devrait étudier l'oxydation en conditions alcalines au peroxydisulfate ($S_2O_8^{2-}$-Cu^{II}) de la lignine de bois de tremble traité à la vapeur et de ses dérivés acétylés et méthylés. Les hémines hydrosolubles méritent d'être étudiées et leur action sur les divers types de lignine disponibles devrait être évaluée tant en milieu aqueux qu'en milieu organique.

S'il s'avère que l'une ou l'autre des méthodes précédentes semble pouvoir augmenter le rendement en précurseurs des éthers méthylliques d'aryles, la recherche devra alors tenir compte du fait que l'aspect le plus important dans l'évaluation du potentiel de mise en marché des éthers alkyliques d'aryles est la nécessité que leur mélange avec des carburants contribue à abaisser la consommation d'essence ainsi que les émissions des véhicules automobiles. La recherche sur la lignine devra donc s'orienter dans une direction permettant de respecter les exigences écologiques de mise en marché des carburants, soit d'une façon spécifique : la réduction des émissions ainsi que la performance et la facilité de conduite des véhicules. Cette dernière direction est valable également pour la recherche sur les éthers méthyliques d'aryles, quelque soit la charge d'alimentation ou la voie de transformation.

Pour orienter les travaux de recherche à venir sur le potentiel de la lignine dans le développement de nouveaux adhésifs, il sera nécessaire de faire une évaluation plus détaillée de la politique et des milieux de règlementation en ce qui a trait aux émissions de formaldéhyde. Si, d'après ces évaluations, il vaut la peine de poursuivre le développement d'adhésifs à base de lignine-PF, il faudra alors démontrer l'applicabilité à l'échelle de l'usine pilote des résultats obtenus; pour ce faire, il faudra préparer suffisamment d'adhésifs de surface en poudre avec durcisseur, assez résistants pour être utilisés dans des panneaux de copeaux, afin de permettre la fabrication de panneaux en vraie grandeur.

Pour les formulations de polymères d'époxyde et de lignine dont la faisabilité technique a été démontrée, il est justifié de procéder à des évaluations pour déterminer si leur production est rentable.

1.0 OBJECTIVES

PART A - FRACTIONATION AND ISOLATION OF LIGNINS FROM STEAM-TREATED WOOD SUBSTRATES

1) Lignin fractions will be isolated by acidification and heat treatment from alkaline extracts of water-washed, steam-treated aspenwood, after the extracts have been fractionated by ultrafiltration.

2) Composition and heterogeneity of the aspenwood lignin fractions will be determined by chemical analysis and compared with unfractionated lignin.

3) A commercial kraft black liquor will be fractionated and the isolated fractions examined, and compared with the lignins from steam-treated aspenwood.

4) Depending on the results obtained with aspenwood and kraft lignins in Parts A and B, a representative softwood residue will be assessed.

PART B - CONVERSION OF LIGNINS TO METHYL ARYL ETHERS, FUELS & PHENOLIC COMPOUNDS (HIGHER VALUE PRODUCTS)

1) The viability of obtaining valuable chemical feedstocks will be determined using (a) oxidative treatments and (b) catalytic hydrogenation (in collaboration with other research groups), on fractionated and unfractionated lignins obtained in Part A.

PART C - APPLICATION OF LIGNIN FRACTIONS AND PRODUCED PHENOLIC FRACTIONS AS ADHESIVES IN THE PANEL PRODUCTS INDUSTRY

1) Thermoset resins for waferboard manufacture will be produced incorporating the lignin-fractions from (A) or phenolic fractions from (B) assessed as having the best potential, and a preliminary evaluation made against the CSA CAN 3-0437-2M standard.

PART D - ECONOMIC ANALYSIS

1) Economic and technical conditions for market entry will be assessed for identified products.

2.0 INTRODUCTION

This report is divided into four sections. Section I contains the work done relating to Part A, B and C of the objectives, except a sub-contract which was added relating to the use of steam-treated lignin in building materials. The report for this sub-contract is in Appendix 4.5. From a review at the end of the first year, it was agreed that this project should concentrate on steam-treated aspenwood lignin and on oxidation processes, therefore, work relating to kraft black liquor (Objective Part A-3 and Part B-1b) and catalytic hydrogenation (Objective Part B,1c) was not undertaken. Section II contains the work related to the modelling of ultrafiltration processes and lignin recovery required under Part D of the objectives. Section III contains an economic analysis of lignin use in wood products adhesives and as fuel octane enhancers to address Part D of the objectives. All conclusions and recommendations are summarized in Section IV.

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SECTION I

FRACTIONATION AND CONVERSION OF LIGNINS FROM STEAM-TREATED ASPENWOOD TO LOW MOLECULAR WEIGHT CHEMICALS AND ADHESIVES

1.0 INTRODUCTION

Canada has vast quantities of lignocellulosic waste available from forest product industries for conversion into fuels and chemicals. Bioconversion systems are technically feasible but high capital and operating costs relative to oil and gas technologies necessitate research and development to reduce the costs and risks.

Steam pretreatment has been shown to be the most economical means of rendering wood susceptible to enzymatic hydrolysis to sugars, which can then be converted to liquid fuels or chemicals. To maximize the cost effectiveness of conversion of biomass to liquid fuels it is essential to utilize the lignin component of any woody feedstock.

Lignins are complex amorphous phenolic polymers. They are present in 16-33% by weight in various woody species. Pretreatment alters the chemical composition and properties of the resulting lignins. Studies of lignins produced from steam-treated aspenwood show that the yields and composition of the lignins isolated are dependent on the pretreatment and recovery procedures used.

Lignins are the major renewable source of phenolic compounds. Over several decades considerable effort has been put into the production of phenolic compounds from lignins, but with limited commercial success. A major reason has been that lignin processing yields a complex mixture of products, the separation costs of which are high. The production of a liquid fuel from the entire product mixture of monomeric phenols and hydrocarbons should be more economically feasible. Lignins can be converted to a mixture of phenolics that can then be transformed into methyl aryl ethers. These ethers are suitable non-metallic octane enhancers, similar in properties to benzene, toluene, and xylene (BTX). The structures of lignins and the chemicals derived from them can also be compared to the phenolic compounds used in the panel products industry. These two end uses suggest that lignin can be exploited as phenol replacements in adhesives for panel products and octane enhancers and fuels. This approach would help to satisfy the fact that several different markets and lignin products will be required to absorb the enormous quantities of lignins that will be available from biomass-to-ethanol plants when this conversion technology is adopted.

A concern in utilization of lignins in polymeric form is the lack of reliable structure, property and performance relationships. The inherent heterogeneity and complexity of lignins has led to products that are deficient in many applications in which petrochemically based products are being used. Petrochemically derived materials are employed because of their homogeneity of chemical functionality and controlled reproducible molecular weight distribution. Lignins have been studied extensively with the goal of replacing phenol in phenol-formaldehyde (PF) resins employed in the panel products industry. In our preliminary evaluation of PF resins with incorporation of different lignins from steam-treated aspenwood, some lignin-fractions were shown to be more desirable than others. Among these were more homogeneous lignin-fractions of lower average molecular weight obtained by fractionation using organic solvents. The production of lignin-fractions that are more homogeneous with controlled properties has been one strategy for producing high value lignin products from waste lignins. The use of several organic solvents to produce homogeneous fractions is probably not commercially viable. Therefore, we proposed to examine the use of ultrafiltration of lignins from steam-treated substrates to produce more homogeneous lignins. Different average molecular weight fractions of a lignin may not only be more suitable for some polymeric applications but also for the production of low molecular weight chemicals.

Several methods of upgrading waste lignins to chemicals have been extensively studied. The methods of interest to us for application to the bioconversion lignins are (a) chemical and electrochemical oxidative methods and (b) mild hydrotreating using catalysts employed for hydrodeoxygenation. In both cases phenolic compounds for the production of methyl aryl ethers and aromatic hydrocarbons can be obtained. More suitable phenolic products may also result that can in the short term be used as PF replacements in the panel products industry.

1.1 ULTRAFILTRATION

Ultrafiltration (UF) is a pressure-driven filtration separation occurring on a molecular scale. Typically, a liquid including small dissolved molecules is forced through a porous membrane. Large dissolved molecules, colloids, and suspended solids that cannot pass through the membrane are retained. This simple procedure requires no phase change, no chemical addition and little energy. Because the transport of matter across an UF membrane involves viscous porous flow, the physical structure of the membrane will control the flow rate and rejection. In practice the process is not that simple and factors outside the membrane may control both solvent flux and rejection. One model envisions the build-up of a cake or gel layer at the upstream membrane surface created by rejection or concentration polarization of the solute or particulate material. This layer then plays a large role in the performance of the filtration process. The pore size of a UF membrane can be characterized by its "molecular weight cut-off" (MWCO). Definitions of MWCO are: the molecular weight below which a species passes through the membrane; or, the molecular weight of a globular solute at which the solute is 90 % rejected by the membrane. These descriptions must be used with discretion, because the shape and the size, as well as electrical characteristics, of the solute are important considerations with respect to species rejection. (For general discussions of UF processes, see for example: Klinkowski, 1983; Paul and Morel, 1981; Applegate, 1984).

Membrane-retained components are collectively called concentrate or retentate. Materials permeating the membrane are called filtrate, ultrafiltrate, or permeate. It is the objective of UF to recover or concentrate particular species in the retentate, or to produce a purified permeate. Diafiltration is a specific UF process in which the retentate is further purified or the permeable solids are extracted further by the addition of water to the retentate.

Ultrafiltration of lignin has been of interest to the pulp and paper industry for two main uses. In the kraft process, while the energy recovery from lignin is key to the economic operation of the kraft mill, many mills currently operate at or above the designed recovery furnace capacity. Removal by UF of some of the lignin present in the black liquor would reduce the heat load on the recovery furnace and relieve the furnace operation (Kirkman, Gratzl and Edwards, 1986; Hill, 1987). The production of purified lignin as a by-product for use in a variety of applications is also feasible.

There has been interest in obtaining high molecular weight lignins for a number of applications. Spent sulfite liquors (SSL) have received most attention (Dubey *et al.*, 1965; Bansal and Wiley, 1975; Claussen, 1978, 1981; Forss *et al.*, 1979; Cox, 1982; Tsapiuk *et al.*, 1989), although filtration of kraft liquors has also been studied (Hill and Fricke, 1984; Uloth and Wearing, 1989). UF has been demonstrated for the production of a lignin fraction, using either kraft lignin or SSL, for use as an extender in PF resin for the manufacture of plywood (Forss and Fuhrmann, 1976, 1978). Fractions of both kraft lignins and lignosulfonates were produced with a wide range of average molecular weights by UF and their properties as dispersants and viscosity reducers were evaluated (Lin and Detroit, 1981). The dependence of the purity of the lignin obtained on the method of ultrafiltration has also been discussed by Claussen (1978).

Ultrafiltration has been considered for the recovery of low molecular weight organic chemicals in the pulping liquors, namely the sugars (Collins *et al.*, 1973) and carboxylic acids (Alén *et al.*, 1986), and for soda recovery (Sapkal *et al.*, 1989). Recently, ultrafiltration was considered for the purification of lignin from kraft liquor for biotechnological applications (Drouin and Desrochers, 1988).

To our knowledge ultrafiltration has not been applied to the lignin-containing alkaline extracts of steam-treated aspenwood.

1.2 CONVERSION TO LOW MOLECULAR WEIGHT CHEMICALS

Conversion of lignins to monomeric compounds has been studied for several decades and this body of work has been comprehensively reviewed by a number of authors (Goheen, 1971, 1981; Goldstein, 1975; Coughlin *et al.*, 1984; Chum *et al.*, 1988). The majority of this work is concerned with conversion of lignin through hydrogenation, hydrocracking, catalytic cracking, pyrolysis and thermolysis. Alkali fusion, hydrolysis, and oxidation have also been used. In general these methods result in the production of numerous compounds whose individual yields are too low to merit commercialization. Work is continuing in a number of laboratories on the conversion and upgrading of lignin to chemicals by thermal and catalytic methods. Under study are alternative methods of using the whole phenolic fraction produced by incorporation into phenolic adhesives (Chum *et al.*, 1989) or by converting them into aryl methyl ethers as octane enhancers (Ratcliff *et al.*, 1988). In contrast, conversion by oxidative methods has not recently received as much attention, despite the fact that vanillin was produced for a period commercially from lignosulfonates

(Goheen, 1971), and that bioconversion lignins are oxidizable to give reasonable yields of monomeric aldehydes.

The oxidation of lignins was thoroughly reviewed by Chang and Allan (1971) but since that time the mechanism of biodegradation of lignins has been elucidated and shown to involve lignin peroxidase and laccase. These enzymes catalyze one electron oxidation of phenolic (laccase and peroxidase), and nonphenolic (peroxidase) groups to give phenoxyl and aryl radical cation radicals and were identified as initial enzymes involved in the cleavages of side chains and aromatic rings of phenolic and nonphenolic moieties of lignins (Higuchi, 1990). Searches for biomimetic models of ligninase have shown that, for example, synthetic iron porphyrins with alkyl hydroperoxide are able to oxidize lignin model compounds (Habe *et al.*, 1985a; Shimada *et al.*, 1987) and also to delignify wood chips (Paszczynski *et al.*, 1988).

As reaction in both chemical and enzymic degradation is initiated by electron transfer, electrochemical oxidation of lignin may provide greater selectivity and means of control. The electrochemistry of lignins has been comprehensively reviewed (Chum *et al.*, 1983; Chum and Baizer, 1985). The reactions are reported to be dependent on the solvent, the supporting electrolyte system, the nature of the electrode materials and other variables. In many investigations, however, neither the materials submitted to electrolytic treatments nor the products were sufficiently characterized. Limited numbers of works dealing with the anodic degradation of lignins have been reported.

One of the ealiest studies was made by Bailey and Brooks (1946). Anodic degradation products consisting of five aliphatic compounds and four aromatic ones were obtained by electrolyzing a butanol lignin from softwood at a lead anode in 1% sodium hydroxide. More recently, Kovalenko *et al.* (1977) reported briefly that a hydrolysis lignin was degraded at various anodes such as platinum, nickel, copper, and graphite in an alkaline anolyte to give small amounts of vanillin and vanillic acid, considerable amounts of carbon dioxide, and mixtures of aliphatic acids.

Limosin *et al.* (1986) studied the oxidation of some lignins on platinum in basic aqueous medium in presence of nitrogen or oxygen. With oxygen a lower deposition on the anode was obtained. The addition of an electron carrier like $K_4Fe(CN)_6$ limited the deposition. A limited analysis was made of the precipitated lignin products. Oxidation lead always to a decrease of the phenyl groups and an increase of the carboxylic groups of the lignins. The benzylic rings were also opened. Shchukin and Babkin (1989) studied the electrochemical oxidation of lignosulfonic acid and model compounds at platinum electrodes and observed also the opening of benzene rings to give dicarboxylic acids.

A series of papers have appeared on the anodic degradation of lignins in alkaline solution (Yoshiyama *et al.*, 1988a, 1988b, 1988c, 1989; Chen *et al.*, 1989). Several different kinds of lignins were electrochemically oxidized at lead and platinum anodes in acidic and alkaline electrolytic solutions. Among the anodes and solutions used, the lead dioxide anode and sodium hydroxide solution were found to be practically the most suitable. About thirty anodic degradation products were detected and analyzed. The product distribution was greatly affected in a complex way not only by the kind of lignin but also by electrolytic conditions such as current density and amount of charge passed.

Utley and Smith (1987) have patented a process for the electrochemical treatment of lignins. Their patent and subsequent paper (Utley, 1988) describe a process for the electrochemical cleavage of lignins at a yield greater than 6%. The electrochemical technique involves passing an electric current through an aqueous alkaline solution of the lignin at a temperature in excess of 100°C whilst maintaining mixing of the solution. The lignin solution is contained in an electrochemical cell adapted to withstand the corrosive effects of hot alkali solution, the temperature and consequent pressure. Utley and his co-workers examined the production of low molecular weight chemicals from organosolv lignins by anodic oxidation. They generally use higher temperatures (170°C) than others (up to 80°C), but most recently employed the presence of nitroaromatics to lower the reaction temperature to ambient (Smith *et al.*, 1989). Preparative scale experiments were not reproducible although the range of phenolic products was generally similar to that produced by conventional nitrobenzene oxidation or high temperature anodic oxidation.

Recently, Löbbecke *et al.* (1990) published a study on the anodic modification of lignins during electrolysis in the Organocell process. Pulping liquor from the five ton/day demonstration plant of Organocell GmbH, Munich, was electrolyzed with different current densities. The analysis of the isolated lignins revealed considerable changes of lignin structure during electrolysis. These changes included polymerization reactions involving the formation of C- and O-condensed interunit linkages and reactions of the side-chain such as decomposition of enol ethers and increase of carboxylic acid (COOH), carbonyl (CO), and aliphatic hydroxyl ($OH_{ali.}$) groups. The extent of the observed reactions was found to be highly dependent on the current density. With the exception of $OH_{ali.}$ groups and residual sugars, the degree of structural modification was inversely proportional to current density.

Finally, it should be noted that the polymeric products from reductive electrolysis of Ethanol-Extracted Explosively-Depressurized Aspen Lignin (EEEDAL) were studied (Chum *et al.*, 1984). The derivative prepared by reaction of EEEDAL and formaldehyde was suggested to replace successfully 25% of phenol in a PF resin (Chum *et al.*, 1985a).

We are unaware of any studies of the biomimetic or electrolytic oxidation of lignins from steam-treated aspenwood lignin.

2.0 MATERIALS AND METHODS

2.1 PREPARATION OF ALKALINE EXTRACT CONTAINING LIGNIN BY STEAM TREATMENT, WATER-WASHING AND ALKALINE EXTRACTION OF THE PREPARED ASPENWOOD

2.1.1 Steam Treatments

Steam treatments were done in a 2-litre pressure vessel closed at both ends by pneumatically actuated ball valves. Commercial, never-dried aspenwood chips were loaded directly into the vessel and after steam treatment (240°C, 100s) were exploded through the lower ball valve into a cyclone. For example, for the first fractionation experiments, steam-treated aspenwood (6.49 kg O.D.) was extracted with water to provide water-insoluble material (SHA-WI) (5.04 kg O.D.).

2.1.2 Lignin Extraction

The general procedure for extraction was as follows. SHA-WI (1.0 kg O.D.) was stirred with aqueous sodium hydroxide (0.4% w/v) at a 5% consistency for 1 hour at room temperature and the resulting product filtered to remove the solid residue. The residue was then extracted a second time by stirring with aqueous sodium hydroxide (0.4% w/v) at a 5% consistency for 30 min and the product filtered a second time. The residue was then washed with the minimum amount of alkali. This provided the alkali extract (35 L) with solids content of 13.4 g/L for the first fractionation.

2.2 FRACTIONATION OF THE ALKALINE EXTRACTS USING ULTRAFILTRATION APPARATUS - BATCH ULTRAFILTRATION

2.2.1 Isolation of Unfractionated Lignin

Unfractionated lignin was isolated for comparative purposes by two methods. Method 1: The extracts were acidified to pH 2.5 with sulfuric acid and the resulting precipitate recovered by centrifugation. The solid recovered was repeatedly washed with water and subsequently air-dried. Method 2: The extracts were acidified as above but then heated to 90°C for 10 minutes by passage of steam. After cooling, the lignin precipitated was recovered by filtration, and washed with water on the filter.

2.2.2 Ultrafiltration

The Amicon TC5E ultrafiltration system was set up to use Amicon Diaflo Ultrafiltration Membranes YM5, YM10, YM30 and YM100.

Alkaline extract (25 L) prepared above (Sections 3.1.1 and 3.1.2) was subjected to ultrafiltration starting with the YM30 membrane (see Figure 1). The retentate was fractionated using the YM100, the filtrate using the YM10, and subsequently YM5 membranes. In all cases an inlet pressure of 60 psi and outlet pressure of 30 psi were maintained. The filtrations were run until the volume retained was reduced to approximately one litre, and after each run dilute alkali was added to wash out the equipment.

In this initial fractionation, the filtrate from the YM10 membrane was rerun through this molecular weight cutoff membrane and the resulting retentate and filtrate added to the appropriate fractions, because of a concern with the state of the membrane on the original run.

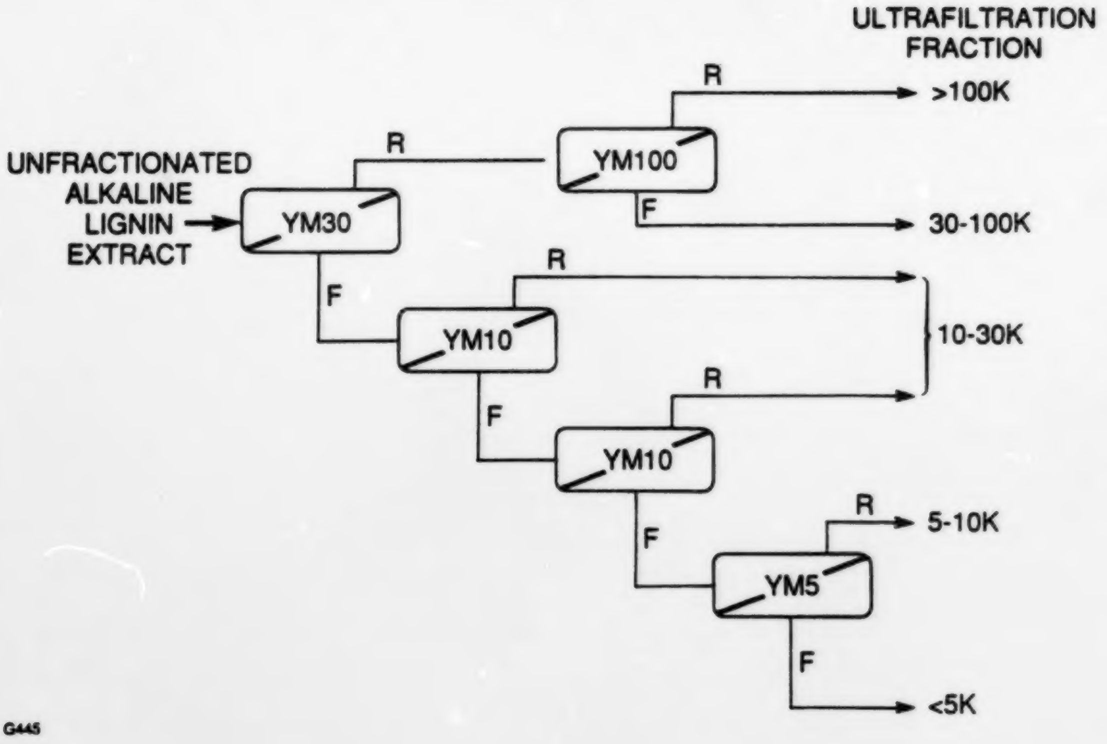
ULTRAFILTRATION FRACTION
UNFRACTIONATED ALKALINE LIGNIN EXTRACT
YM30
R
F
YM100
R
>100K
F
30-100K
YM10
R
YM10
R
10-30K
F
YM5
R
5-10K
F
<5K
G445

Figure 1 Schematic of First Ultrafiltration Experiment on Alkaline Extracts from Water-Washed Steam-Treated Aspenwood; R represents Retentate, F represents Filtrate

The resulting filtrates and the retentate from the YM100 were divided in two and the lignin precipitated from each using methods 1 and 2 above.

Using the same procedure as in the first ultrafiltration experiment 25 L of alkaline extracts prepared as in Sections 3.1.1 and 3.1.2 were fractionated (see Figure 2). The filtrations were run each time until the retentate volume was reduced to approximately 300 mL. After each run a limited volume of alkali was used to rinse out the equipment and added to the appropriate fraction.

The retentates and filtrate from the YM5 fractionation were divided into two samples and the acid precipitable lignin recovered by the two methods described above.

2.2.3 Production of Lignin-Fractions for Concordia University (Sub-contract)

Lignin (155.5 g O.D. wt) was recovered by acidification, heat treatment and filtration from a fraction (20 L) of an alkaline extract of steam-treated aspenwood (240°C, 100s). A further fraction (60L) of the alkaline extract was subjected to ultrafiltration using membranes in the order YM 100, YM 30, and YM 10 to produce four fractions. The filtrations were run each time with some limited addition of water until the retentate volume was reduced to 1-2 L. The water additions were made because of the thickening of the retentate and low filtration flows. Precipitation was as for the unfractionated extract.

2.2.4 Analysis of Products in Supernatant Solution after Recovery of Lignin from the YM 10 Filtrate Produced in the Fractionation for Concordia

An aliquot (1 L) from the supernatant solution (10 L) resulting after the acidification and recovery of lignin from the YM 10 filtrate produced in the fractionation of material for Concordia (Section 3.2.3) was continuously

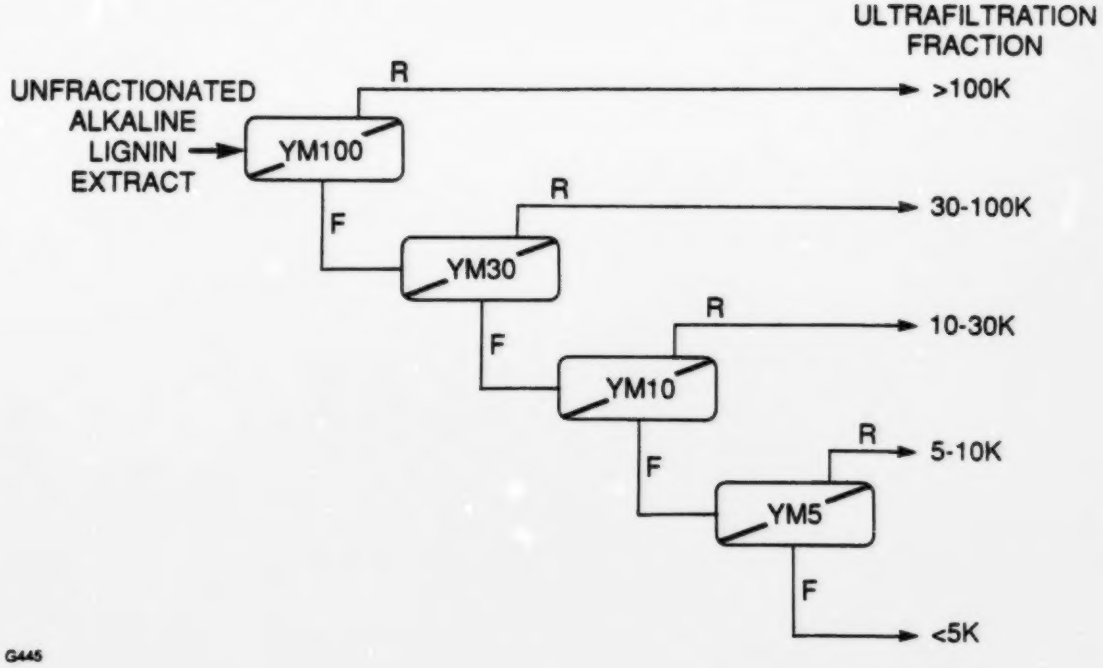
ULTRAFILTRATION FRACTION
UNFRACTIONATED ALKALINE LIGNIN EXTRACT
YM100
R
>100K
F
YM30
R
30-100K
F
YM10
R
10-30K
F
YM5
R
5-10K
F
<5K
G445

Figure 2 Schematic of Second Ultrafiltration Experiment on Alkaline Extracts from Water-Washed Steam-Treated Aspenwood; R represents Retentate, F represents Filtrate

extracted with ethyl acetate (225 mL). Then an aliquot of the extraction solvent (25 mL) was dried and evaporated, yielding 0.51 g (20.4 mg/mL) of solids. Analysis by gas chromatography - mass spectrometry (GC/MSD, see Section 3.5.6 below) was made of the ethyl acetate extract from the supernatant solution and the p-hydroxybenzoic acid present quantified by single ion monitoring (SIM).

2.3 FRACTIONATION OF THE ALKALINE EXTRACTS USING ULTRAFILTRATION APPARATUS - MULTIPLE BATCH VERSUS CONSTANT VOLUME ULTRAFILTRATION

2.3.1 Preparation of Alkaline Extracts for Experiments

Aspenwood chips were steam-treated at 240°C for 100 s, water-washed and alkali extracted as previously described to provide 80 L of alkaline extracts with a solids content of 11.3 g/L.

2.3.2 Precipitation of a Sample of Unfractionated Lignin from the Alkaline Extracts

Lignin (5.5 g) was recovered from the alkaline extracts (1 L) by acidification with sulfuric acid, heating to 90°C, and filtration.

2.3.3 Extraction of Starting Lignin to Determine How Much Material Soluble in Ethyl Acetate and Diethyl Ether

Samples of unfractionated lignin were subjected to Soxhlet extraction with ethyl acetate or diethyl ether to determine the amount of material present that was soluble in these solvents. The lignin contained 11.5 % and 1.2 % soluble material, respectively.

2.3.4 Precipitation of Starting Alkaline Extract in the Presence of Ethyl Acetate

To determine the feasiblity of precipitating the starting lignin in the presence of ethyl acetate and thereby removing low molecular weight fraction, an aliquot of the alkaline extract (1 L) was stirred with ethyl acetate (0.2 L) and then acidified to a pH of 2.5. Some precipitation of lignin took place, but this floated to the top in the organic phase once stirring was stopped. The organic phase was dark black in color, while the aqueous phase was orange. The solution was filtered to collect the precipitate. The filtrate was collected, and the organic phase separated, dried and evaporated to dryness. The organic phase yielded 1.92 g of a viscous tarry solid. The lignin precipitate collected by the filtration was dried to yield 4.70 g of a black powder. This material was not powdery or fluffy in appearance like lignin recovered by acid precipitation. Based on this experience it was decided to precipitate the lignin for the second part of the fractionation experiment in the normal manner and subject it to a normal soxhlet extraction.

2.3.5 Constant Volume Ultrafiltration (Diafiltration)

The ultrafiltration system was set-up in the normal manner but with a reservoir tank to feed under siphon into the primary feed tank. With two 100K MWCO membranes in place the feed tank was filled with the alkaline black liquor (17 L) and the reservoir connected. The filtration was then run until 2.5 times the initial volume of fresh 0.4 % alkali (42.5 L) had been added from the reservoir. The retentate was precipitated in the normal manner and the lignin yield determined. The filtrate was concentrated by roto-evaporation to 4.3 L, and subjected to a similar process but using the 30K MWCO membranes and 2.5 times the original volume, i.e. 10.75 L. Unfortunately, during this step a membrane appeared to rupture, therefore the filtration was stopped, the filtrate and retentate combined and reconcentrated, and the process restarted. The filtrate was concentrated to run through the 10K MWCO membranes but the flow rate was so low that this stage was abandoned. Therefore the retentate and filtrate from the 30K membranes were precipitated to give yields of lignin-fractions.

2.3.6 Multiple Batch Ultrafiltration

With the two 100K MWCO membranes in place the feed tank was filled with the alkaline black liquor (17 L). The filtration was then run until the volume in the tank was reduced to 4 L. Fresh alkali (17 L) was then added and the volume reduced again to 4 L. This procedure was repeated once more. The lignin in the retentate was then precipitated in the normal manner, and the combined filtrates concentrated to 11.8 L. This was then batch filtered using the 30K MWCO membranes reducing the volume at each time to 3 L and making up with a fresh 9 L of alkaline solution. This addition was made 3 times. Lignin fractions were then recovered from the combined filtrates and the retentate in the usual way.

2.4 FRACTIONATION OF ALKALINE EXTRACTS USING ULTRAFILTRATION APPARATUS - CONSTANT VOLUME FILTRATION OF THE ETHYL ACETATE-EXTRACTED LIGNIN

2.4.1 Preparation of Ethyl Acetate-Extracted Lignin

Lignin (96.1 g O.D.) was precipitated from a portion of the alkaline extract (17 L) (prepared as described previously) by acidification, heating at 90°C for 10 min, then cooling and subsequently recovering the lignin by filtration.

The precipitated lignin was extracted with ethyl acetate using a Soxhlet apparatus. After the extraction was complete the solvent extracts were concentrated by rotoevaporation and finally dried under vacuum to yield extractable material (14.06 g). The extracted lignin residue was air-dried and the yield determined (80.0 g O.D.).

2.4.2 Preparation of Alkaline Solution of Extracted Lignin

Attempts were made to redissolve the ethyl acetate extracted lignin (80 g) in aqueous sodium hydroxide (0.4 %). Attempts were made to dissolve some of the sample in higher concentrations of alkali. Complete dissolution of the lignin could not be achieved, therefore the insoluble material (14.1 g) was removed by a combination of filtration and centrifugation. The resulting solution of lignin in 0.4 % aqueous sodium hydroxide was used in the ultrafiltration experiment.

2.4.3 Ultrafiltration Experiment - Constant Volume (Diafiltration)

The ultrafiltration system was set-up in the normal manner but with a reservoir tank to feed under siphon into the primary feed tank. With two 100K MWCO membranes in place the feed tank was filled with the alkaline solution of ethyl acetate-extracted lignin (15 L) and the reservoir connected. The filtration was then run until 2.5 times the initial volume of fresh 0.4 % alkali (37.5 L) had been added from the reservoir. The retentate was precipitated in the normal manner and the lignin yield determined. The filtrate was concentrated by roto-evaporation to 10.0 L, and subjected to a similar process but using the 30K MWCO membranes and 2.5 times the original volume, i.e. 25 L. The retentate and filtrate from the 30K membranes were precipitated to give yields of lignin-fractions.

2.4.4 Solubility of Ethyl Acetate-Extracted Lignin in Alkaline Solution with Added Phenol

Samples of ethyl acetate-extracted lignin (0.4 g, M.C. 5%) and differing amounts of phenol (0.01 - 0.1 g) were added to sodium hydroxide (0.4% w/v, 100 mL) at room temperature and stirred for 60 min. After this period the resulting mixtures were filtered, the precipitate collected dried under vacuum at 50°C, and weighed. A similar experiment using the ethyl acetate-solubles of the lignin, instead of phenol, could not be done because the vacuum-dried extractable material would not redissolve in the alkaline solution.

2.5 CHARACTERIZATION OF ISOLATED LIGNINS, LIGNIN-FRACTIONS, ELECTROLYSIS PRODUCTS AND LOW MOLECULAR WEIGHT CHEMICALS

2.5.1 Ethyl Acetate Extractions

Vacuum-dried unfractionated lignin and fractions recovered from the second ultrafiltration experiment by method 2 were extracted with ethyl acetate for 22 h using a Soxhlet apparatus. The ethyl acetate extracts were then rotoevaporated to dryness and finally dried under vacuum at 50°C. The ethyl acetate insoluble residues were also dried under vacuum at 50°C.

2.5.2 Total Hydroxyl Group Content

Total hydroxyl contents were determined by acetylation using acetic anhydride-pyridine followed by titration of the unused reagent (Browning, 1967).

2.5.3 Molecular Weight Distribution Determinations

Molecular weight distribution data were determined by high performance size exclusion chromatography (HPSEC) (Himmel *et al.*, 1983; Himmel *et al.*, 1984; Pellinen and Salkinoja-Salonen, 1985). Four Ultrastyragel columns (Waters) were used in series, 1000 Å, linear, 500 Å, and 100 Å. Detection was made using UV detector at 254 nm and a refractive index detector. The solvent used was THF at a flow rate of 1.0 mL/min and a temperature of 30°C. Data was collected and processed with the Waters 840 data station using the Waters Expert chromatography software. Calibration was achieved using monodisperse polystyrene standards (Supelco) and low molecular weight compounds.

Samples were quantitatively acetylated for HPSEC using the method of Chum *et al.*, (1985b), which recovers the whole acetylated lignin sample by azeotropically removing the excess reagent and solvent as opposed to alternative procedures which recover the acetylated lignin by precipitation in water and can lead to loss of low molecular weight components.

2.5.4 Infrared Spectroscopy

Infrared absorption spectra of lignins and electrolysis products were recorded on a Nicolet 5DX FTIR spectrophotometer after pelletization in KBr. Typically, lignin (2.5 mg) and KBr (350 mg) were ground together using an agate mortar and pestle, in air. To record some spectra a Pye Unicam SP1100 Infrared Spectrophotometer was used.

2.5.5 ^{13}C NMR Spectroscopy

^{13}C NMR spectra were recorded on a Varian XL-300 spectrometer operating at 75.43 MHz for ^{13}C, using a 10 mm multinuclear probe. The solvent for all spectra was dimethyl sulfoxide-D_6, which was also used for internal reference (39.80 ppm). The acquisition time was varied according to sample solubility, the number of transients collected being from 13,000 to 20,000. The spectra were normally recorded using 50 mg of lignin in 0.5 mL of solvent.

2.5.6 Gas Chromatography - Mass Spectrometry

Gas chromatographic - mass spectrometry (GC-MS) analyses were performed on a HP 5890 gas chromatograph interfaced to a HP 5970 mass selective detector (MSD). Typically a DB-1 fused silica column was used with helium as carrier gas. The split-splitless injector was used typically in the split mode. Crude extracts were analyzed after reaction with Trisil (Pierce Chemical Co.) to convert hydroxyl and carboxylic acid groups to trimethylsilyl derivatives or after acetylation with acetic anhydride-pyridine (1:1). Purified materials were analyzed underivatized, silylated or acetylated. Quantification of selected individual components was performed by single ion monitoring (SIM).

2.5.7 Nitrobenzene Oxidations

Nitrobenzene oxidation of the lignin samples was performed according to the method of Pepper *et al.* (1962) and Chau and Wayman (1979). The products were analyzed by GC-MSD and SIM was used for quantification.

2.6 ANODIC OXIDATION OF STEAM-TREATED ASPENWOOD LIGNINS

To familiarize ourselves with the operation of the electrolysis equipment purchased, a trial electrolysis was made of 1,2-dimethoxybenzene in methanol/potassium hydroxide using platinum electrodes, following the procedure of Weinberg and Belleau (1973). Current - potential curves were satisfactorily determined and a preparative electrolysis followed by GC-MSD. Satisfactory production of 1,2,4-trimethoxybenzene was observed, one of the expected major products.

For the anodic oxidation of the lignins the electrolysis conditions used are similar to those of Yoshiyama *et al.* (1988a) and product isolation is a modification of Utley and Smith (1987) and Bailey and Brooks (1946). General procedures are described below.

2.6.1 Equipment

The following basic components for electrochemical experiments were obtained (all produced by Electrosynthesis Co.); a potentiostat controller Model 410 and power supply Model 420A, a coulometer Model 640, and a standard H-type cell with a porous frit divider (Model C-600) and a standard H-type cell (Model C-200) that could be used undivided or with membrane dividers (for example NAFION). A range of electrode materials; Pt, high purity graphite (GR12), graphite felt (GFS5, GFS6), glassy carbon (GLCR-10), Foametal nickel (FM100), and lead dioxide on titanium, and reference electrodes (Sargent-Welch) were also obtained.

2.6.2 Electrolysis

An H-type divided glass cell with a medium porosity sintered glass diaphragm was used. The anode (2.5 x 2.0 cm) was selected from foametal nickel, glassy carbon, or lead dioxide. A platinum plate (2.6 x 2.0 cm) was used as the cathode. The electrolysis solution (anolyte, 50-70 mL, containing lignin 100-120 mg, and catholyte, 30-35 mL) was 1M sodium hydroxide. Electrolysis was potentiostatically controlled, the applied potential (versus saturated calomel electrode) for the experiment being determined by construction of current - potential curves. The applied voltage was usually in the 0.5 - 0.6 V range at approximately 25 mA/cm^2 current density.

2.6.3 Product Recovery

After passage of the required charge the anolyte was acidified, any precipitated lignin collected by filtration, and the resulting supernatant solution extracted with chloroform. The aqueous solution of anolyte was then evaporated to dryness and the resulting solids were extracted with acetone. The organic extracts were dried over magnesium sulfate, evaporated to dryness, and analyzed by GC/MSD.

2.6.4 Procedure for Investigation of Electrolysis Parameters in the Electroysis of Lignins, Runs S1-S13

In these experiments the general procedures as outlined above were used. Modifications were as follows. The electrolysis cell was placed for the runs in either thermostatically controlled oil bath (70°C) or water bath (25°C). These baths would not allow magnetic stirring of the cell contents and therefore agitation by the inlet of the gas under which the electrolysis was to be run was used. In these experiments a gas inlet was added to the anolyte compartment that extended down into the anolyte. The cell was then flushed prior to and during the run with either air or nitrogen as required at 10-15 mL/min. In runs S1-S3, an gas exhaust line was set up from the cell containing tared charcoal and ascerite gas absorption traps. Problems with moisture in the lines was circumvented by installing anhydrous calcium chloride moisture traps before and after these traps in subsequent experiemnts when the gas traps were required.

When different operating conditions to those originallly selected were needed current versus potential curves were constructed for the different conditions to be investigated, i.e.:

1. [NaOH] 1 M, 25°C (Control)
2. " + 0.1 g lignin
3. " + 1.0 g lignin
4. [NaOH] 3 M, 25°C (Control)
5. " + 0.1 g lignin

6.	"	+ 1.0 g lignin	
7.	[NaOH] 1 M, 70°C		(Control)
8.	"	+ 0.1 g lignin	
9.	"	+ 1.0 g lignin	
10.	[NaOH] 3 M, 70°C		(Control)
11.	"	+ 0.1 g lignin	
12.	"	+ 1.0 g lignin	

2.6.5 GC-MS Analysis of Ethyl Acetate Extracts

The ethyl acetate extracts of the supernatant solutions obtained after acidication of the alkaline reaction mixtures of electrolyzed lignin and recovery of the precipitable product were prepared for GC-MS analysis as follows. Internal standard (xylitol) in methanol was added to known amounts of the extract, the methanol removed by rotary evaporation, and the residue derivatized with bis(trimethylsilyl)trifluoroacetamide (BSTFA):trimethylchlorosilane (TMCS):pyridine (1.0:0.05:2.0). The resulting solution was analyzed directly by GC-MS. GC-MS analyses for these materials were performed on a Hewlett Packard 5890 GC equipped with a HP 5970 mass selective detector. A methylsilicone column (HP Ultra2 25m x 0.20 mm ID x 0.33 micron film thickness) was used with a linear carrier gas (helium) velocity of 35 cms^{-1}. The initial column temperature of 100°C is held for 0.5 min after which the temperature is ramped up to 285°C at the rate of 15°C min^{-1} and held at this final temperature for 7.2 min. Under these conditions, the retention times of the n-alkanes are: nC11 4.00 min, nC12 4.92 min, nC13 5.86 min, nC14 6.92 min, nC15 7.78 min, nC16 8.62 min, nC18 10.18 min, nC19 10.93 min, nC20 11.64 min, nC21 12.32 min, nC22 12.98 min, nC23 13.64 min, nC24 14.37 min, nC25 15.20 min, nC26 16.14 min, nC27 22.36 min.

Response factors for hydroxy acids and diacids were determined by duplicate injections of seven samples of a mixture of standards.

2.6.6 Analysis of Alkaline Electrolysis Liquors

The method described by Alén *et al.* (1984) was adapted for use in the analysis of hydroxyacids and diacids in the alkali solutions of electrolysis products. According to this method, samples (1 mL electrolysis liquor containing about 10 mg electrolyzed lignin and breakdown products) are passed through a column of weakly acidic cation-exchange resin (Amberlite IRC-50, NH_4^+ form, 10 to 15 mL wet volume) using water as eluant to obtain a final volume of 50 mL. Internal standards (xylitol and benzyl alcohol, 0.5 mg each) are added and the solutions taken to dryness on a rotary evaporator. The dry residue is derivatized with 1 mL of reagent (pyridine:BSTFA:TMCS, 1:0.5:0.025) at room temperature with occasional shaking for at least 30 minutes. The resulting solution is analyzed directly by GC-MS.

2.7. OXIDATION OF LIGNIN USING PEROXYDISULFATE, ($S_2O_8^{2-}$-Cu^{II}), IN ACETIC ACID

2.7.1 Oxidation Procedure Using ($S_2O_8^{2-}$-Cu^{II}) in Acetic Acid

Lignin (0.200 g O.D.), ammonium persulfate (0.456 g, 2 mmol) and cupric acetate (0.199 g, 1 mmol) were placed in a test-tube with a magnetic stirrer and acetic acid:water (5:1) (6 mL) added. Reactions run under nitrogen were flushed with nitrogen for ten min prior to sealing the tubes. All reactions were run in sealed tubes. Controls were made up in the same manner, except for the omission of the persulfate salt. Reactions were initated by placing the sealed tubes in an oil bath at the required temperature. After the required run time they were removed and quenched in a cold water bath. After cooling, the reaction tubes were opened and the contents washed out into a tared centrifuge bottle with water (50 mL). After, stirring for ten min, the contents were centrifuged to allow separation of the precipitated reaction product and the supernatant liquid. After removal of the supernatant liquid, the precipitate was washed with water (20 mL), and the process repeated. The washed precipitate was dried overnight in a vacuum oven, and the yield determined. The supernatant and washings were combined, extracted with chloroform, dried over magnesium sulfate, evaporated to dryness, and yield determined.

2.7.2 Preparation of Acetylated Lignin (AcSEL) for Oxidation Reactions

Lignin (2.5 g) was weighed into a test-tube with a stirring bar and pyridine:acetic anhydride (1:1) (100mL) added. The tube was flushed with nitrogen and sealed. The reaction vessel was then heated at 50°C for 20 h, with stirring. The acetylated lignin was recovered by pouring the acetylation mixture into cold water with stirring. The product was recovered by filtration and washed repeatedly with water, and dried *in vacuo* at 60°C. The yield was 2.81 g of acetylated lignin.

2.7.3 Preparation of Methylated Lignin (MeSEL) for Oxidation Reactions

Lignin (2.5 g) was dissolved in 30% aqueous sodium hydroxide (35 mL) and while the solution was stirred vigorously in an atmosphere of nitrogen at a temperature of 60°C, dimethyl sulfate (25 mL) was added dropwise over a period of 1 h. The solution was allowed to stand overnight at room temperature, heated to boiling, cooled, and acidified with dilute hydrochloric acid. The precipitated lignin was recovered by filtration, washed with water and dried *in vacuo* over phosphoric anhydride. The product was purified by precipitation from 90% acetic acid into water. After drying, the yield of methylated lignin was 1.81 g.

2.7.4 Molecular Weight Distributions of Persulfate Oxidized Lignins

Molecular weight distributions were determined by gel permeation chromatography on a series of ultrastyragel columns (10^3, 500, linear, 100 Å) calibrated with narrow polystyrene standards. Tetrahydrofuran (THF) stabilized with 250 ppm BHT was used as eluant at a flow rate of 1 mL min^{-1}. The unmodified lignin and precipitated reaction products produced from it were acetylated using the procedure of Chum *et al.* (1985b). The MeSEL and AcSEL and the precipitated reaction products therefrom, were completely soluble in THF and required no further derivatization. Acetylated and methylated lignin samples were dissolved in THF to give approximately 0.5% solutions. Duplicates of each sample were analyzed using 50 microliters per injection. A UV detector was used at 254 nm.

2.8. OXIDATION OF LIGNIN MODEL COMPOUNDS USING METALLOPORPHYRINS

Oxidation reactions were attempted using the following commercially available catalysts:

Hemin,	bovine {chloroprotoporphyrin IX iron(III)}
TPPFeCl,	{5,10,15,20-tetraphenyl-21*H*,23*H*-porphine iron(III) chloride}
TPPMnCl,	{5,10,15,20-tetraphenyl-21*H*,23*H*-porphine manganese(III) chloride)}
TPPCu,	{5,10,15,20-tetraphenyl-21*H*,23*H*-porphine copper(II)}
TPPVO,	{5,10,15,20-tetraphenyl-21*H*,23*H*-porphine vanadium(IV) oxide}.

The procedure used was based on that of Shimada *et al.* (1984a). The standard complete reaction system contained 5μmoles of the model compound, 10μmoles of *tert*-butyl hydroperoxide as the active oxygen donor, and 0.5μmoles of the metalloporphyrin in dichloromethane (1 mL). The reaction mixtures lacking either the catalyst or the active oxygen donor were taken for controls. Both complete and control reaction systems were stirred magnetically at room temperature under air for 20 h. The reaction mixtures were then evaporated with a stream of nitrogen, dichloromethane (100 μL) added, and the soluble material analyzed by gas chromatography.

2.9 EVALUATION OF FRACTIONATED LIGNINS IN ADHESIVES FOR WOOD COMPOSITE PANELS

2.9.1 Lignins

Seven samples of steam-treated aspenwood lignin were used. These were the unfractionated lignin, the fractions from the multiple batch ultrafiltration (<30K, 30-100K, >100K), and the fractions from the constant volume ultrafiltration (<30K, 30-100K, >100K). A sample of a softwood kraft lignin was obtained from a local pulp and paper mill.

2.9.2 Phenol-Formaldehyde Resin

A low molecular weight PF resin was prepared by reacting phenol and formaldehyde in a 1.0 to 2.2 molar ratio at a temperature of 65°C following a procedure similar to that described by Chiu (1984). This low molecular weight PF was mixed with a commercial PF resin W 3154 ML supplied by Borden Chemicals in a 35:65 ratio a solids basis. The final resin mixture had a pH of 10.4 and a Brookfield viscosity of 98 cps at a 47.3 % solids content compared to a viscosity of 1500 cps for the unmodified W 3154 ML resin at 46.5 % solids content. Figure 3 shows the size exclusion chromatograms of the commercial and experimental PF resins used in this study. This commercial PF resin (W 3154 ML) was selected as it already contains a mixture of high and low molecular weight PF and was found to work well as a crosslinker for lignosulfonates (Calvé *et al.*,1988). The low molecular weight PF was added to

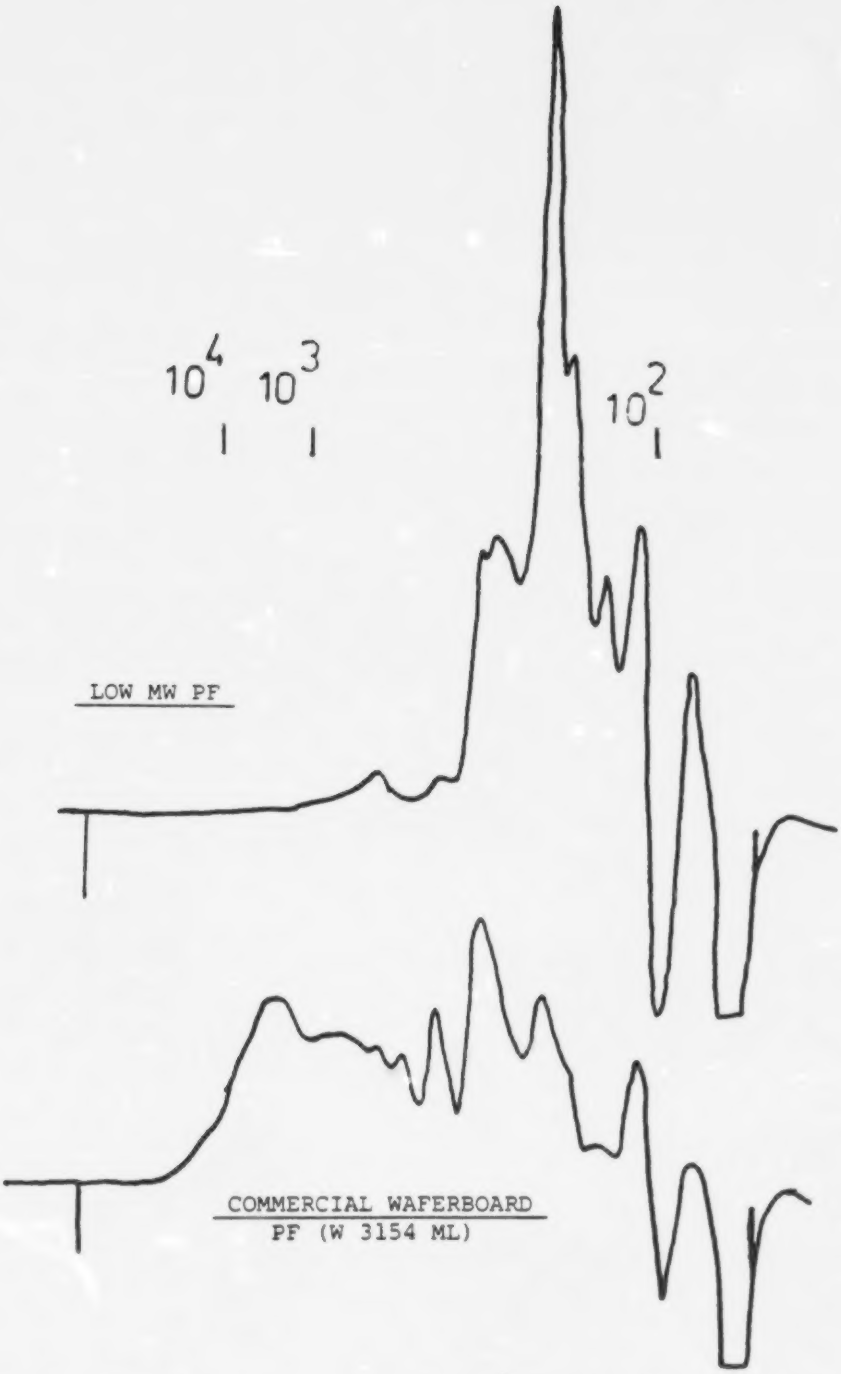

Figure 3 Size Exclusion Chromatography of Commercial PF and Low Molecular Weight PF Resins: Differential Refractive Index Detector Response as a Function of the Molecular Weight Relative to Poly(oxyethylene). Ultrastyragel 100, 500 Å Columns with Tetrahydrofuran/0.4 % Trichloroacetic acid at 25°C as Eluant

the commercial PF to lower its viscosity and facilitate its application onto the wood particles.

2.9.3 Lignin-Phenolic Resins

Lignin-phenolic resins containing 10, 20, 30 and 40 % lignin (on solids basis) were prepared.

In a typical example, unfractionated aspenwood lignin powder (2.0 g) was dispersed in concentrated ammonium hydroxide (8.0 g) and then simply blended with the phenol-formaldehyde crosslinker (as prepared in section 3.7.2) (6.4 g) at 47.3 % solid content. The resulting lignin (40 %) - PF (60 %) resin was stirred 16 h to assure the complete solubilization of the material. The adhesive was sprayed onto the wood particles using a nozzle with a small opening to assure a good distribution of the resin. It was important that no insoluble material be present in the liquid resin solution, which could plug the nozzle. The high molecular weight lignin-fractions (>100K) obtained by ultrafiltration could not be dissolved even in a solution of concentrated ammonium hydroxide-phenol-formaldehyde and thus could not be evaluated. The heat treatment used in the recovery of the lignins could be responsible for the condensation and insolublization of these lignin-fractions. In fact, the reason for using concentrated ammonium hydroxide as solvent was to solublize the lignin. An excess of sodium hydroxide would reduce the adhesive properties of the resin while ammonium hydroxide is a fugitive base and most of it is removed during the moisture content adjustment when the resin coated wood particles are exposed to hot air.

2.9.4 Particleboard Preparation and Testing

The adhesives were evaluated by production and evaluation of particleboard. Poplar wood particles were obtained by hammermilling veneers. The fractions which passed through a 4.75 mm Tyler sieve but were retained on a 1.18 mm sieve were used for the study. A large batch of wood particles was sprayed with 1.5 % molten wax in a 0.6 m^3 laboratory blender. Subsequently, the coated particles were dried at 105°C and after cooling were stored at room temperature in the presence of dessicant. For the preparation of particleboards, the dry wood particles were sprayed in a 0.06 m^3 blender with 16.7 g of adhesive at 30 % solids (5 % adhesive solid based on dry wood). The moisture content of the resin coated particles was then adjusted to 5 % by hot air drying. The resin coated particles were then handfelted into a 35 x 69 mm mold and pressed in an electrically heated press with 11.1 mm stops at 210°C for 3 or 5 minutes. This press time included the 50-s press closing time. Two replicate boards were prepared for each set of variables evaluated at a target density of 720 kg/m^3.

2.10 EVALUATION OF STEAM-TREATED LIGNIN AS A "PRE-CURE" RESISTANT SURFACE ADHESIVE FOR THREE-LAYER WAFERBOARD

2.10.1 Lignins

Eight types of steam-treated lignins were prepared for evaluation as thermosetting waferboard adhesive extenders. The aspenwood lignins were prepared as indicated in Table 1.

2.10.2 Phenol-Formaldehyde Resin

The lignins as prepared were lumpy in texture and required the use of a mortar and pestle to reduce them to a consistent fine powder. Fifteen g of each lignin type was dissolved in 73.5 g liquid phenol formaldehyde (PF) (W3154 M provided by Borden Chemical) with constant stirring. The W3154 resin is a binary type of phenolic resin which contains both high and low molecular

Table 1

List of the Various Aspenwood Steam-Treated Lignins used in This Study

Lignin Type	Preparation
RS1	80s/240°C, acid precipitated, heated
RS2	100s/240°C, acid precipitated, heated
RS3	1.6% SO_2, 100s/200°C, acid precipitated, heated
RS4	1.6% SO_2, 100s/200°C, acid precipitated, heated
RS5	Acetone-soluble fraction[a] of RS3 1.6% SO_2, 100s/200°C, acid precipitated, heated
RS6	10-30K fraction from ultrafiltration of alkaline extracts of 100s/240°C, acid precipitated, heated
RS7	30-100K fraction from ultrafiltration of alkaline extracts of 100s/240°C, acid precipitated, heated
RS8	>100K fraction from ultrafiltration of alkaline extracts of 100s/240°C, acid precipitated, heated

[a] Acetone-soluble fraction represents 62% by wt. of RS3

weight phenol-formaldehyde. The PF was 47% solids content which allowed for a PF/lignin ratio of 70:30. The pH of the viscous mixture maintained at 10.0 with concentrated ammonium hydroxide. Typically, the mixture required about 5 g of ammonium hydroxide to complete dissolution. 1.5 g of ammonium sulfate or (3% x the solids of the mixture) was dissolved in 36.5 g of water. This solution was added slowly to the lignin PF mixture which was again maintained at pH 10.0 with ammonium hydroxide (about 10 g). The lignin-PF mixture was reduced to 30-35% solids with distilled water, and spray-dried in a laboratory spray dryer (Bowen Engineering). The spray dryer inlet was maintained at 190°C and the outlet at 90°C.

The lignin-PF powders were evaluated for chemical thermosetting properties using, as preliminary screening tests, cure stroke and fusion test. Although these are not official tests they are used extensively in the waferboard industry. A description of each test method is appended, (Appendix 4.1).

As the RS4 material was considered close to the commercial control it was further modified using the same formulation described with the addition of 4.5% ammonium sulfate as opposed to 3%. The resultant spray-dried powder yielded similar properties as the BD802 (Reichhold Ltd.) control (39 s, 31 mm) see Table 39, Section 3.6.

2.10.4 Waferboard Preparation and Testing

The RS4-PF with the 4.5% ammonium sulfate was used to prepare experimental laboratory 760 x 380 x 11.1 mm homogeneous waferboards. The panels were divided in the middle so that each panel pressed yielded a 380 x 380 x 11.1 mm lignin panel and a 380 x 380 x 11.1 mm control panel. Commercial BD802 powder was used as the control. The blending and pressing parameters are listed in Table 2. The lignin-PF adhesive was evaluated by pressing using three press cycle times 3, 4, and 5 minutes, and 3 replicates were made for each press

Table 2

Process Parameters for Experimental Homogeneous Waferboard Panels Prepared with Steam-Treated Lignin-PF and Commercial PF Controls

Panel size:	380 x 380x 11.1 mm
Panel target density:	650 kg/m^3
Wax content:	1.5%
Resin content:	2.0% (lignin-PF or BD802)
Moisture content:	4.0%
Press temperature:	210°C
Press pressure:	3.45 Mpa
Press close time:	50 s
Press decompression:	15 s

time. The waferboard panels were evaluated following test procedures found in the CSA standard CAN 3-0437.0-M85 "Test Methods for Waferboard and Strandboard". The tests considered included: Modulus of Rupture (MOR), Modulus of Elasticity (MOE), Modulus of Rupture after 2 hour boil (wet MOR), and Internal Bond (IB).

A commercial waferboard face resin must be able to resist precuring since it is closest to the not press platens. The precure resistance of the lignin-PF adhesive was compared to the commercial BD802. In order to test the resistance of the adhesive to pre-cure a caul plate heated in an oven at 205°C and then placed on the prepared three layer waferboard mat for five min under 25 kg weight. The mat was then pressed in a normal manner using a 4 min press cycle time. Blending and pressing parameters are given in Table 3.

3.0 RESULTS AND DISCUSSION

3.1 FRACTIONATION, ISOLATION AND CHARACTERIZATION OF LIGNINS FROM STEAM-TREATED WOOD SUBSTRATES

3.1.1 Batch Ultrafiltrations

From 5 L of the alkaline extracts prepared for the first ultrafiltration experiments 36.2 g (O.D.) of lignin was recovered by acidification and ultrafiltration (method 1), and from 2.5 L of the extracts 17.4 g (O.D.) of lignin by acidification, heating to 90°C and filtration (method 2).

The solution volumes used in the first ultrafiltration experiment with the Amicon ultrafiltration system and the membranes YM100, YM30, YM10, and YM5 are

Table 3

Process Parameters for Experimental Three Layer Waferboard Panels Prepared for the "Pre-Cure" Resistance Study

Panel size:	380 x 380x 11.1 mm
Panel target density:	650 kg/m^3
Face:core:face ratio	20:60:20
Wax content:	1.5%
Resin content:	2.0% (lignin-PF or BD802)
Core resin content:	2.5% (commercial IB947 core resin)
Moisture content:	4.0%
Press temperature:	220°C
Press pressure:	3.45 Mpa
Press cycle time:	4 min
Press close time:	50 s
Press decompression:	15 s

shown in Table 4. The yields of lignins precipitated by the two recovery methods are shown in Table 5.

The total sum of the lignin fractions isolated by method 1 (69.9 g) and method 2 (64.8 g) indicate a loss in yield of lignin in comparison to the expected yield from unfractionated alkaline extracts, 90.5 g and 87.0 g respectively. Part of this loss may be due to the differences in concentration of lignin in the various fractions and the original extracts (Venter and Van der Klashorst 1989). The extra acidification required to precipitate the fractions containing the lowest molecular weight lignins is also of concern.

Molecular weight distribution data for the unfractionated and fractionated lignins isolated by both methods were obtained by HPSEC analysis of the acetylated derivatives. The results are summarized in Table 6. In this series only a small difference was observed between the molecular weight data for the unfractionated lignins isolated by the two methods. Likewise, there were only small differences in the data obtained for the fractionated lignins with the exception of the 30-100 K fractions. Molecular weight distribution curves obtained by UV detection are shown in Figures 4 and 5. These show polydisperse fractions were obtained and a substantial low molecular weight component was present particularly in the portion of the highest average molecular weight fraction solubilized by acetylation. As shown in Figure 5 the ultrafiltration step using the 5K MWCO membrane did not achieve any discrimination on the basis of molecular weight.

The fractionation process was repeated to determine the reproducibility of the separation and recovery procedures. Using the same procedure as in the first ultrafiltration experiment 25 L of alkaline extracts were fractionated. From 4 L of the initial alkaline extract 28.8 g (O.D.) of lignin was produced by method 1 and 27.3 g (O.D.) by method 2. The yields of recovered lignin fractions are given in Table 7, with the results for the first fractionation

Table 4

Summary of Solution Volumes Used in First Ultrafiltration Experiment of Alkaline Extracts From Water-Washed Steam-Treated Aspenwood

Feed Solution	Volume (L)	Membrane cutoff(K)	Rinse Volume (L)	Volume Filtrate (L)	Volume Retentate (L)
Starting solution	25	30	3	27.15	0.785
<30K	25	10	1.5	24.76	1.74
<10K	24	5	1.25	23.18	2.07
>30K	10	100	3	11.88	1.22
5-10K	5	10	2	1.04	6.09

Table 5

Yields of Precipitated Lignins Obtained from First Ultrafiltration Experiment Using Alkaline Extracts from Water-Washed Steam-Treated Aspenwood

Fraction	Isolation Method	Yield lignin (g)	% solution used for ppt.	Corrected yield (g)
>100K	1	12.19	89.2	13.7
	2	9.69		10.9
30-100K	1	20.7	89.2	23.2
	2	19.7		22.1
10-30K	1	19.5[a]	80	24.4
	2	19.0[a]		23.8
5-10K	1[b]	1.1[a]	75.5	1.46
	2[b]	1.7[a]		2.25
<5K	1[b]	5.55[a]	77.8	7.13
	2[b]	4.47[a]		5.74

[a] air dried yield (Moisture contents usually 2-3%)
[b] acidified to pH 1.5

Table 6

Molecular Weight Distribution Data Obtained for Lignin-Fractions Recovered in First Ultrafiltration Experiment

Fraction	Precipitation Method 1				Precipitation Method 2			
	U.V.		R.I.		U.V.		R.I.	
	M_n	M_w	M_n	M_w	M_n	M_w	M_n	M_w
Unfractionated	656	5934	975	6398	559	5275	867	6350
>100K[a]	377	5566	665	6390	336	3937	571	4830
30-100K	339	3323	616	5480	966	9219	1710	10259
10-30K	504	3303	876	4537	462	3198	748	4510
5-10K	379	4608	543	2082	358	1213	492	1890
<5K[b]	378	1227	571	2462	324	1150	487	2073

[a] Material only partially solubilized by acetylation

[b] Approx. 5% of acetylated sample insoluble in THF

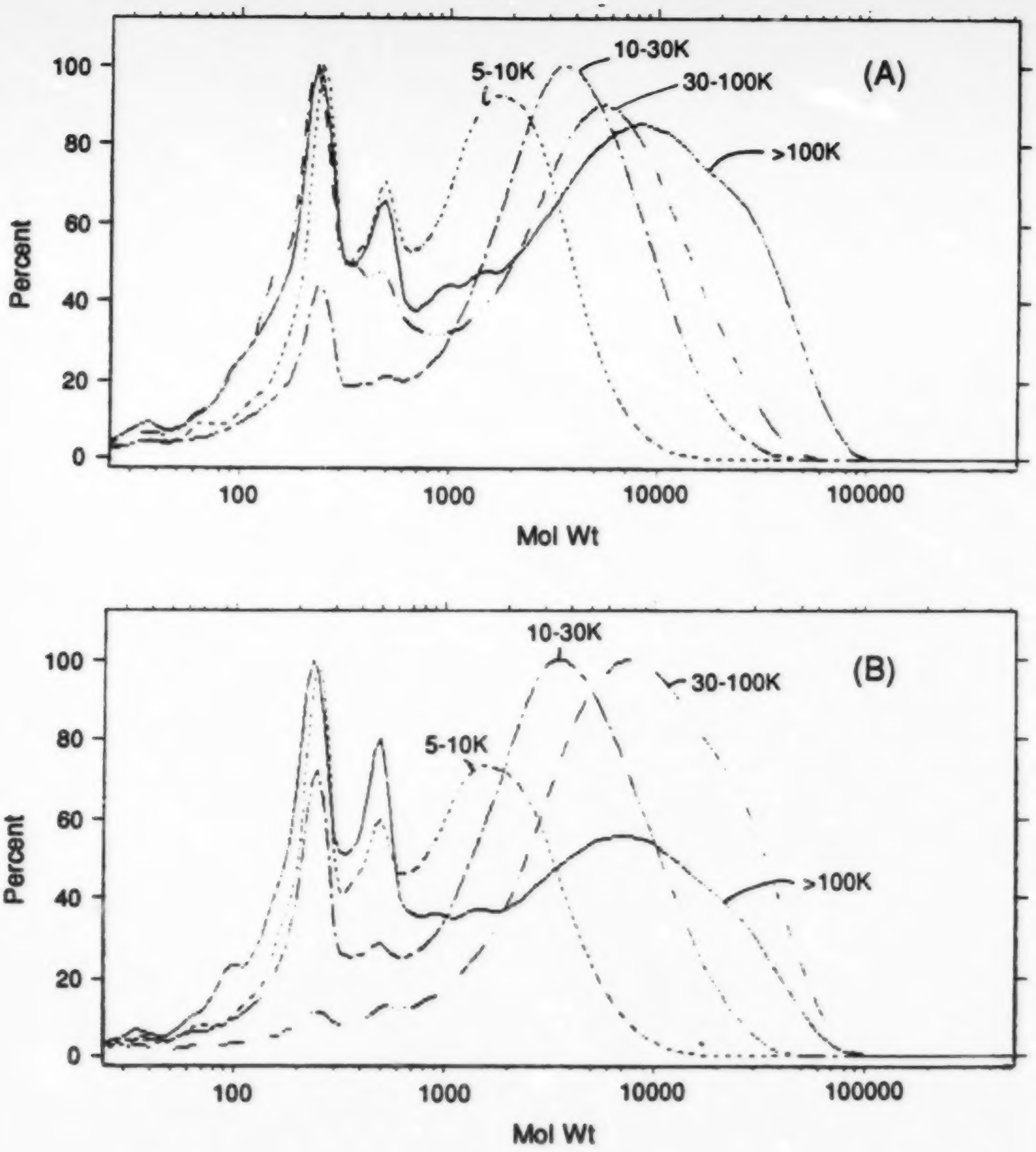

Figure 4 Molecular Weight Distributions (Polystyrene Equivalents) for Lignin-Fractions (>100K, 30-100K, 10-30K, 5-10K) Recovered in First Ultrafiltration Experiment. (A) Method 1, (B) Method 2. (UV detection)

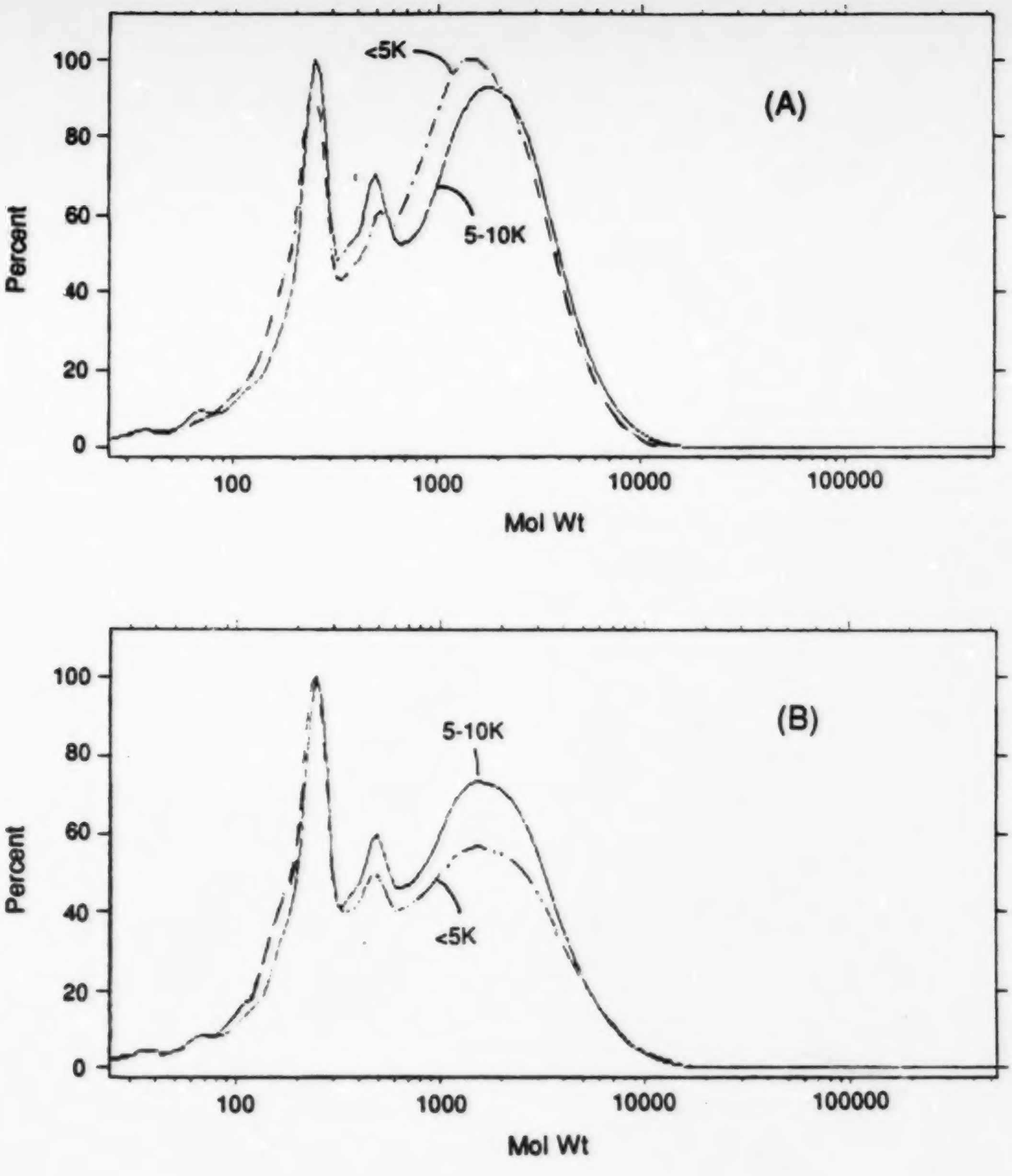

Figure 5 Molecular Weight Distributions (Polystyrene Equivalents) for 5-10K and <5K Lignin-Fractions Recovered in First Ultrafiltration Experiment. (A) Method 1, (B) Method 2. (UV detection)

Table 7

Yields of Precipitated Lignins Obtained from Second Ultrafiltration Experiment Using Alkaline Extracts from Water-Washed Steam-Treated Aspenwood

Fraction	Method 1			Method 2		
	g (O.D.)	%[a]		g (O.D.)	%[a]	
>100K	16.0	17.7	(15.1)[b]	17.2	20.1	(12.5)
30-100K	29.0	32.2	(25.6)	28.2	33.0	(25.4)
10-30K	18.3	20.3	(26.9)	16.8	19.6	(27.4)
5-10K	4.4	4.9	(1.6)	6.4	7.5	(2.6)
<5K	7.5	8.3	(7.9)	4.0	4.7	(6.6)
Total	75.2	83.4	(77.2)	72.6	84.9	(74.5)

[a] % of lignin yield obtained from unfractionated alkaline extract.

[b] Values for first fractionation as a % of lignin yield obtained from unfractionated alkaline extract in parentheses.

in parentheses.

As previously observed, there was a loss in total yield in recovery of lignin after fractionation in comparison to unfractionated material. The reason for this loss in yield is not immediately obvious, as in this second fractionation the argument of differences in lignin concentration in the alkaline fractions after filtration and the original extracts cannot be used.

Molecular weight distribution data for the unfractionated and fractionated lignins from the second ultrafiltration experiment are summarized in Table 8. In this series, unfractionated lignins of higher average molecular weight were isolated by method 2, as we had found in previous research when heating of the acidified extracts was used to produce a filterable lignin product. The average molecular weight of the lignin recovered in this precipitation method is probably partially related to the duration of the heating step used after acidification.

The molecular weight data for the isolated fractions was as expected from the first ultrafiltration experiment. Unfortunately, the analytical technique used is unsuitable for the highest molecular weight fraction (>100K).

Total hydroxyl group determinations were made on the isolated lignins from the second fractionation by the acetylation procedure described by Browning (1967). The results are given in Table 9. The values are the average of triplicates or quadruplicates. In each case the values obtained for the >100K fraction were always nonsensical and the reason was unknown, therefore a calculated value is also given. The hydroxyl content decreases with decreasing molecular weight.

Infrared spectra have been recorded for the lignin-fractions from the second fractionation. The spectra of the unfractionated lignins recovered by the two

Table 8

Molecular Weight Distribution Data Obtained for Lignin-Fractions Recovered in Second Ultrafiltration Experiment

Fraction	Method 1				Method 2			
	U.V.		R.I.		U.V.		R.I.	
	Mn	Mw	Mn	Mw	Mn	Mw	Mn	Mw
Unfractionated	548	4032	1120	5210	612	4999	1204	6169
>100K[a]	373	6844	1012	8032	368	5531	891	6272
30-100K	779	6751	1621	7711	534	5873	1233	7139
10-30K	552	3102	1199	4189	383	2566	889	3687
5-10K	270[b]	882[b]	596[b]	1649[b]	391	1856	836	3220
<5K	301	809	616	2165	373[b]	1227[b]	736[b]	2179[b]

[a] Material only partially solubilized by acetylation.

[b] Approx. 5% of acetylated sample insoluble in THF.

Table 9

Results (% wt) for Total Hydroxyl Determinations for Lignins-Fractions Recovered in Second Ultrafiltration Experiment

Fraction	Method 1	Method 2
Unfractionated	9.7	10.5
>100K[a]	4.0 (11.5)[b]	24.6 (11.7)[b]
30-100K	10.2	10.7
10-30K	8.9	9.4
5-10K	7.4	9.4
<5K	8.4	9.3
Vanillin (Standard 11.18 %)	11.2	11.0

[a] Samples not soluble in acetylation mixture.

[b] Value in parentheses calculated from fraction yields and hydroxyl values of other fractions and unfractionated lignin.

precipitation methods are shown in Figure 6. Inspection of these spectra indicate only slight differences between the lignins.

The starting lignin and the five fractions obtained by method 2 in the second ultrafiltration run were characterized by IR and ^{13}C NMR spectroscopies. Samples of the unfractionated lignin and the five fractions were extracted with ethyl acetate using a Soxhlet apparatus. The yields of ethyl acetate soluble material are given in Table 10.

The IR spectra were recorded of the unextracted lignins, ethyl acetate-insoluble residues and ethyl acetate-solubles (Figures 7-12). Table 11 presents peak assignments of the absorbance bands for the unfractionated lignin based on those proposed by Schultz and Glasser (1986) and Owen and Thomas (1989). The spectra for the fractions as isolated from ultrafiltration (Figure 7) show variations in the absorption bands resulting from aliphatic C-H (2934, 2836, 1335 cm^{-1}), C=O (1737-1704 cm^{-1}), C-O phenol (3410 and 1121 cm^{-1}), and C-H isolated H on aromatic ring (916, 842 cm^{-1}). The spectra from the <5K and 5-10K fractions have greater intensity in the bands resulting from carbonyls.

In Figures 8-12 are presented the IR spectra of the five fractions and their corresponding ethyl acetate-soluble and -insoluble components. The IR spectra for the insoluble residues are similar for the <5K, 5-10K, and 10-30K fractions, and for the 30-100K and >100K fractions. These results suggest that it may be inappropriate to fractionate this lignin into as many as five fractions. The spectra of the extracted components have important absorbances at 2934,1720, and 842 cm^{-1}. The carbonyl band intensity is increased in the 5-10K and >100K fractions. The intensity of the C-H band of adjacent hydrogens on an aromatic ring increased with increasing molecular weight of the original lignin-fraction.

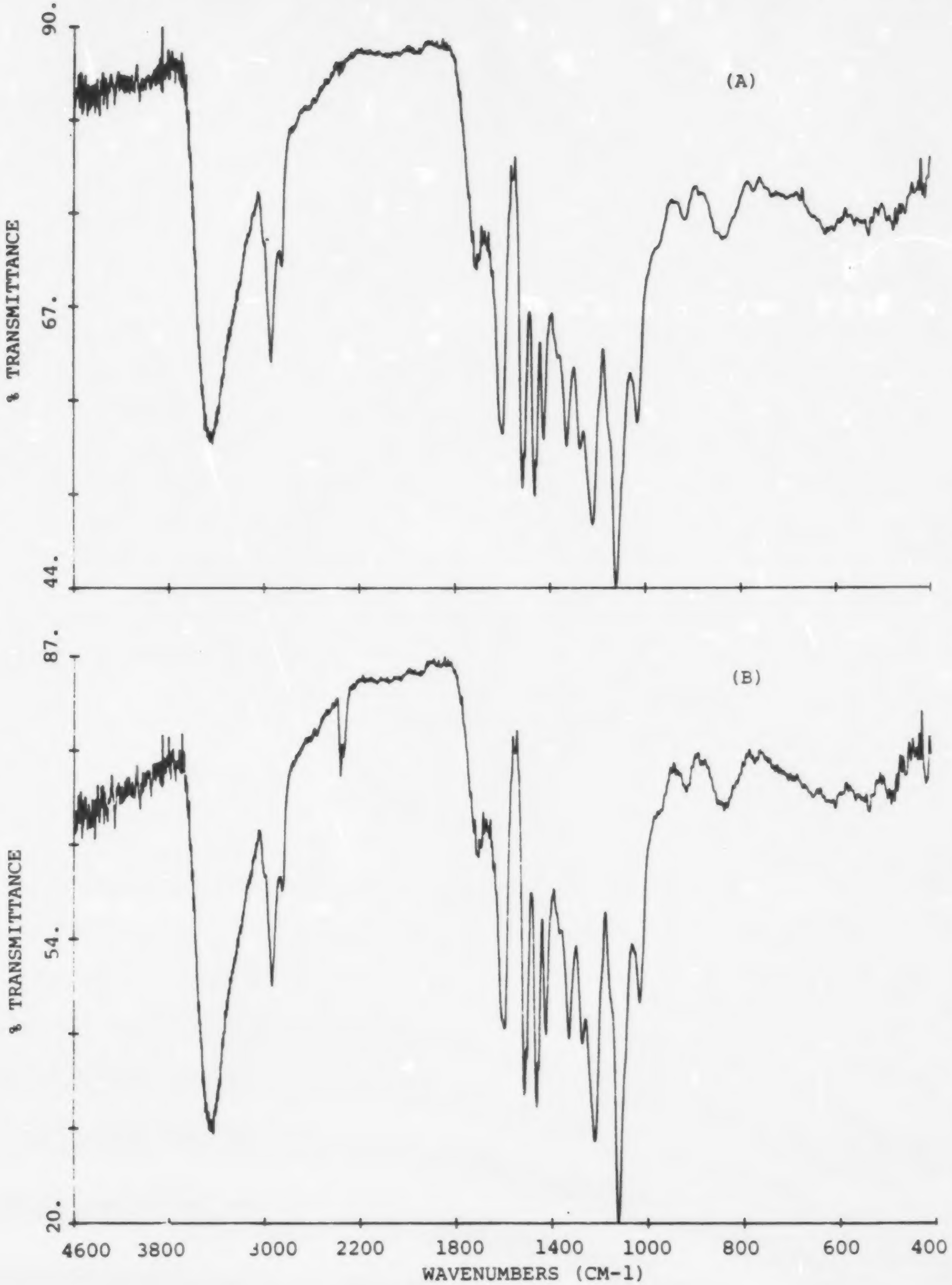

Figure 6 IR Spectra of Unfractionated Lignin Recovered in Second Ultrafiltration Experiment by (A) Method 1, (B) Method 2

Table 10

Yields of Ethyl Acetate-Solubles from Unfractionated Lignin and Lignin-Fractions Isolated By Method 2 in Second Ultrafiltration Experiment

Fraction	Yield[a] (% wt)
Unfractionated	26
>100K	22
30-100K	6
10-30K	7
5-10K	18
<5K	37

[a] Average of two determinations

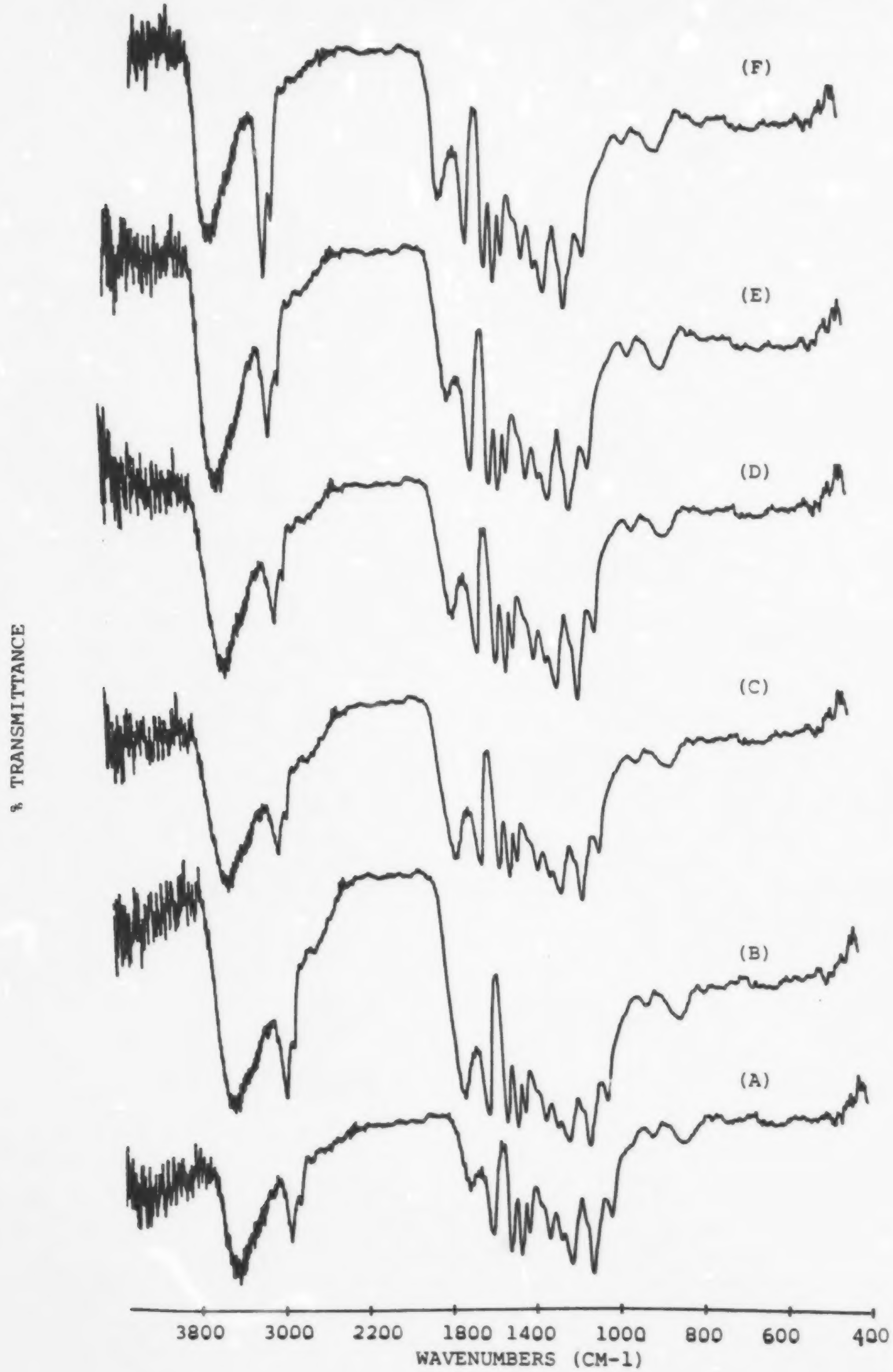

Figure 7 IR Spectra of Unfractionated Lignin and Lignin-Fractions Isolated By Method 2 in Second Ultrafiltration Experiment. (A) Unfractionated, (B) <5K, (C) 5-10K, (D) 10-30K, (E) 30-100K, (F) >100K

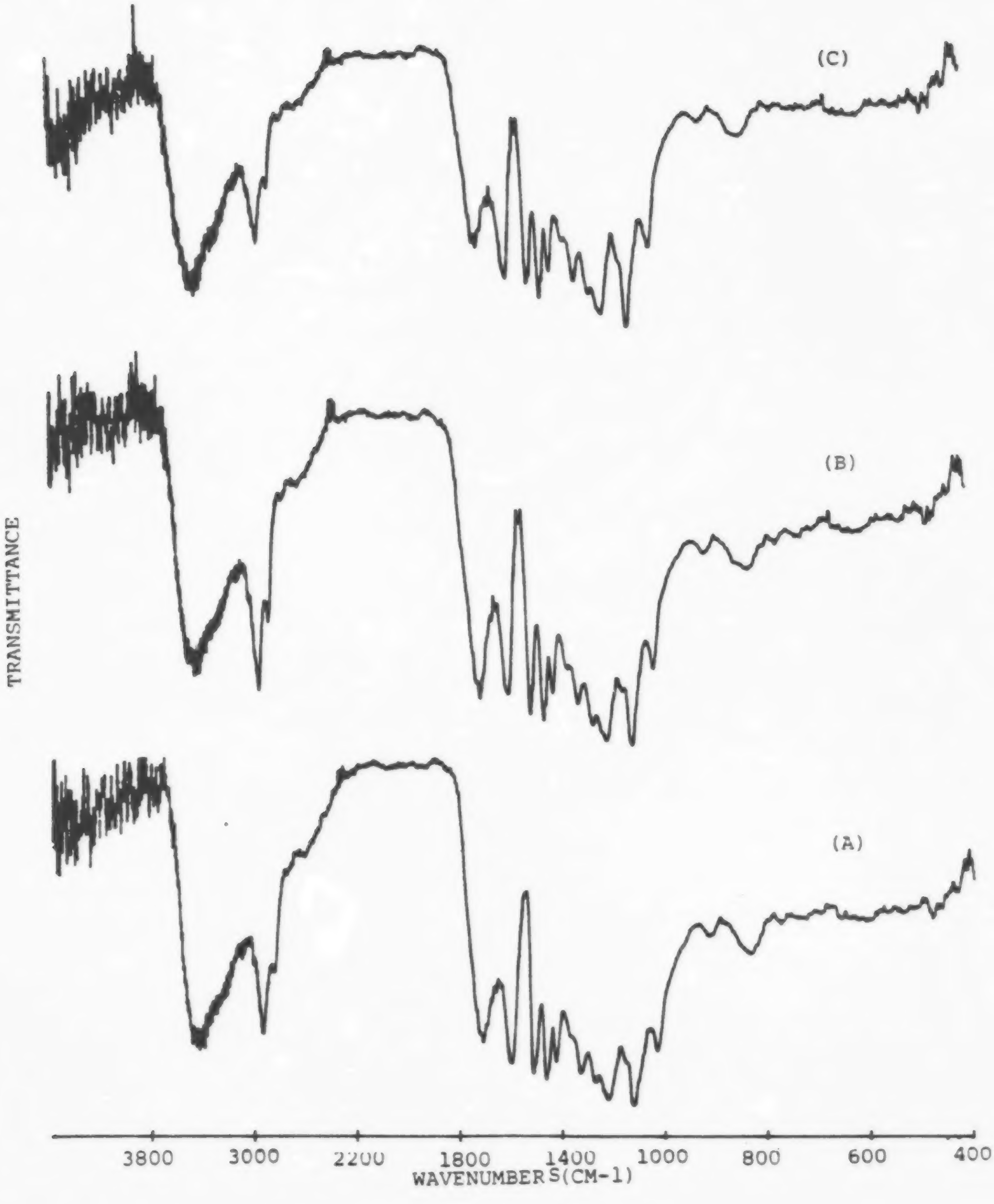

Figure 8 IR Spectra of <5K Lignin-Fraction Recovered in Second Ultrafiltration Experiment. (A) Unextracted, (B) Ethyl Acetate-Solubles, (C) Ethyl Acetate-Insolubles

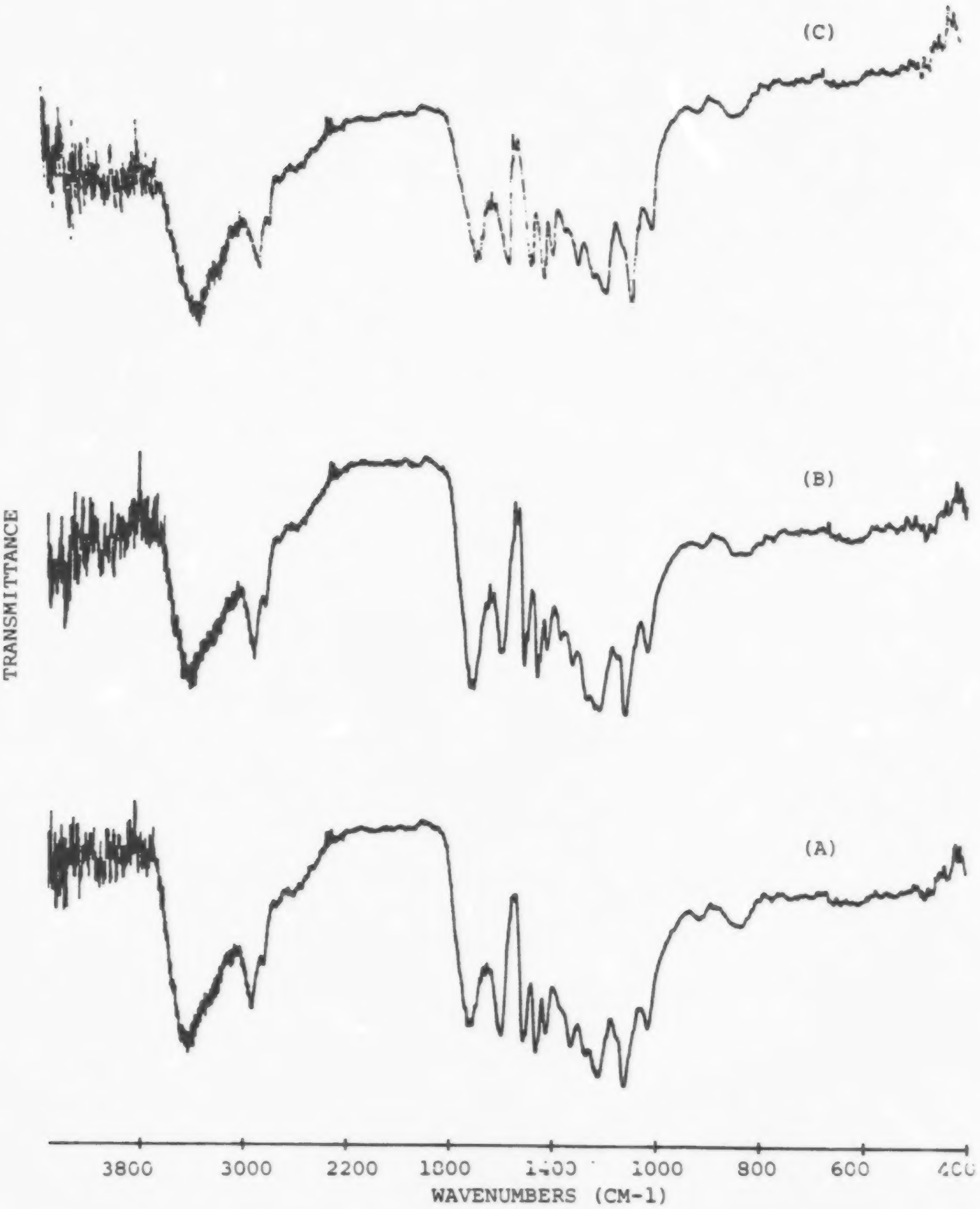

Figure 9 IR Spectra of 5-10K Lignin-Fraction Recovered in Second Ultrafiltration Experiment. (A) Unextracted, (B) Ethyl Acetate-Solubles, (C) Ethyl Acetate-Insolubles

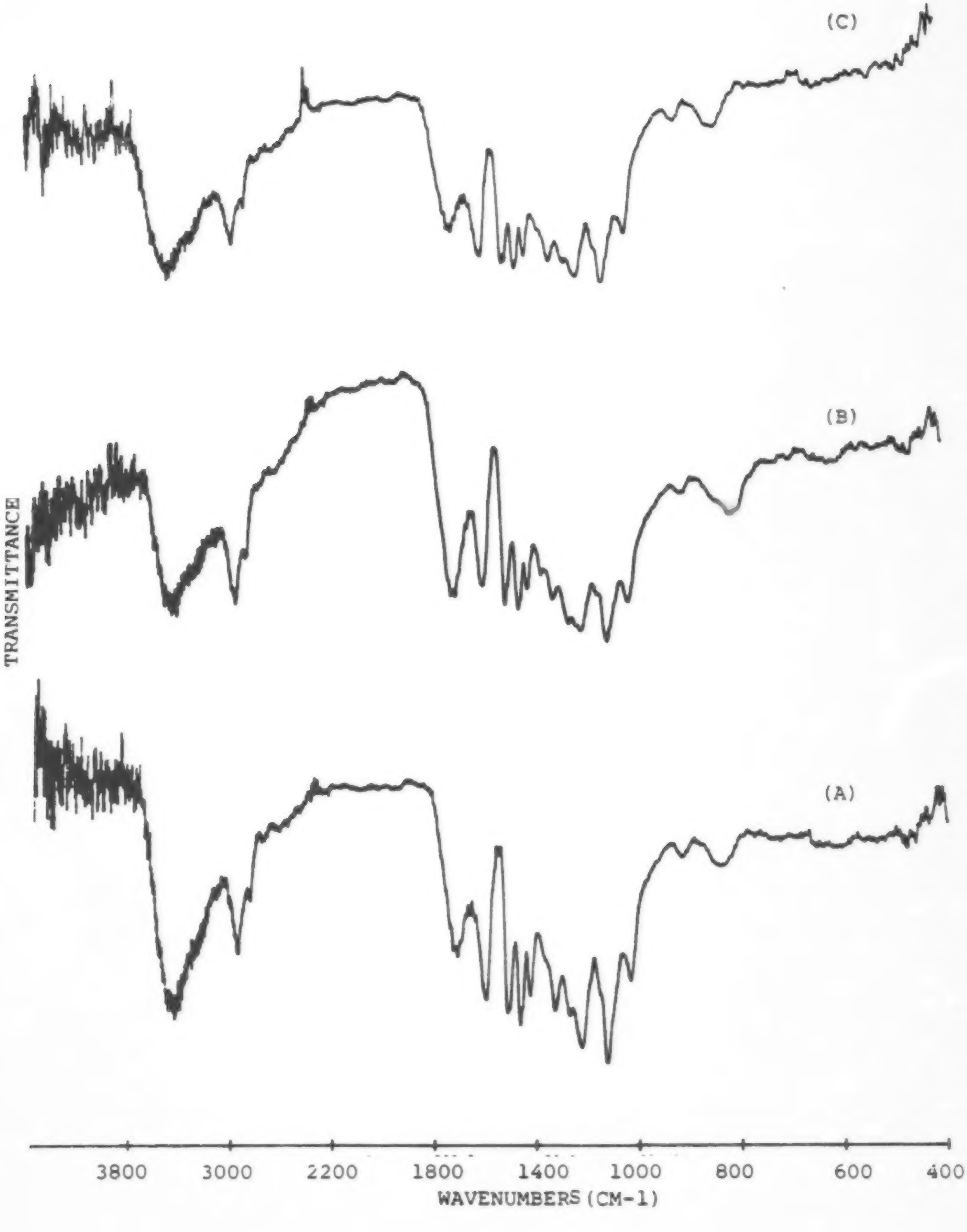

Figure 10 IR Spectra of 10-30K Lignin-Fraction Recovered in Second Ultrafiltration Experiment. (A) Unextracted, (B) Ethyl Acetate-Solubles, (C) Ethyl Acetate-Insolubles

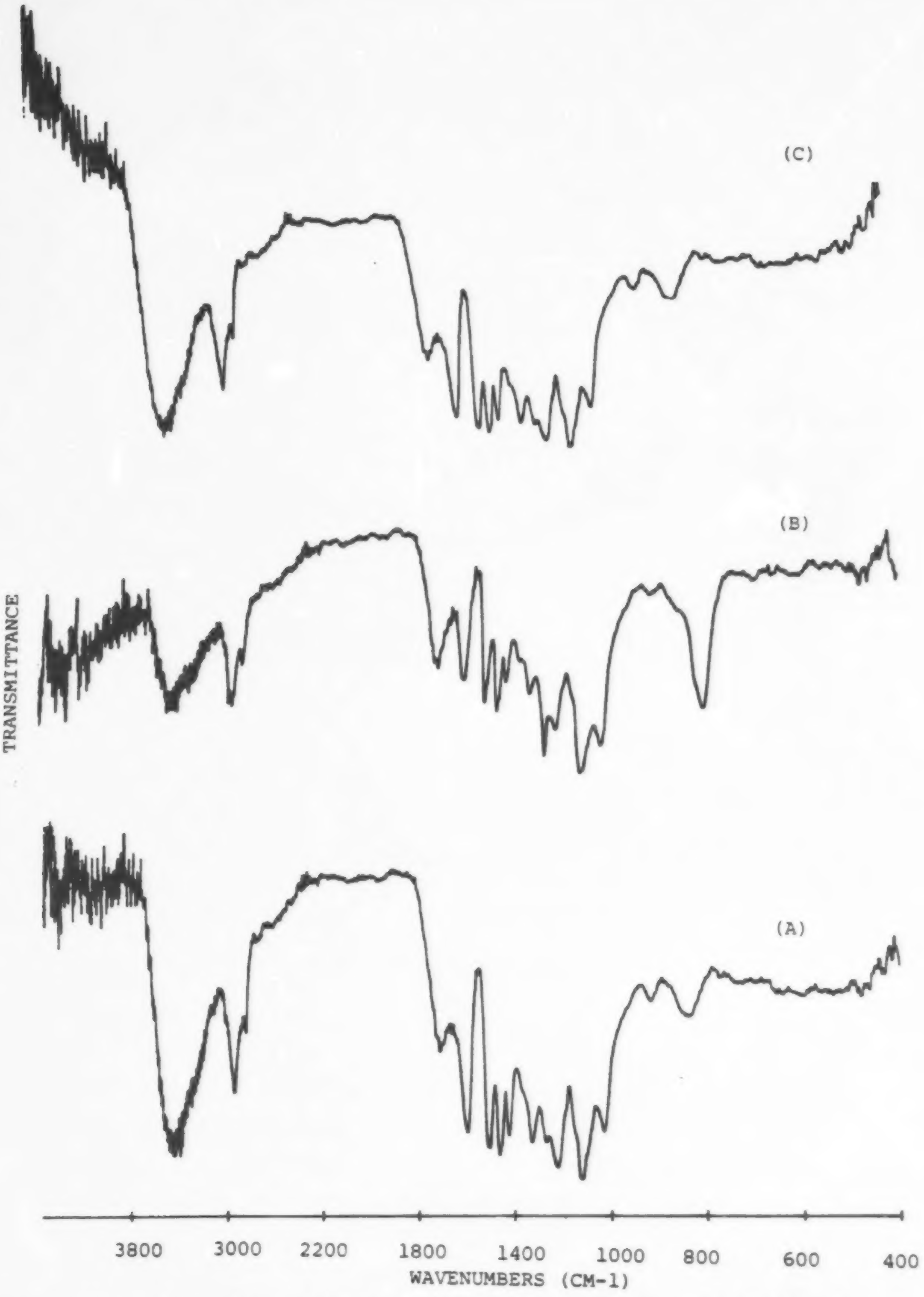

Figure 11 IR Spectra of 30-100K Lignin-Fraction Recovered in Second Ultrafiltration Experiment. (A) Unextracted, (B) Ethyl Acetate-Solubles, (C) Ethyl Acetate-Insolubles

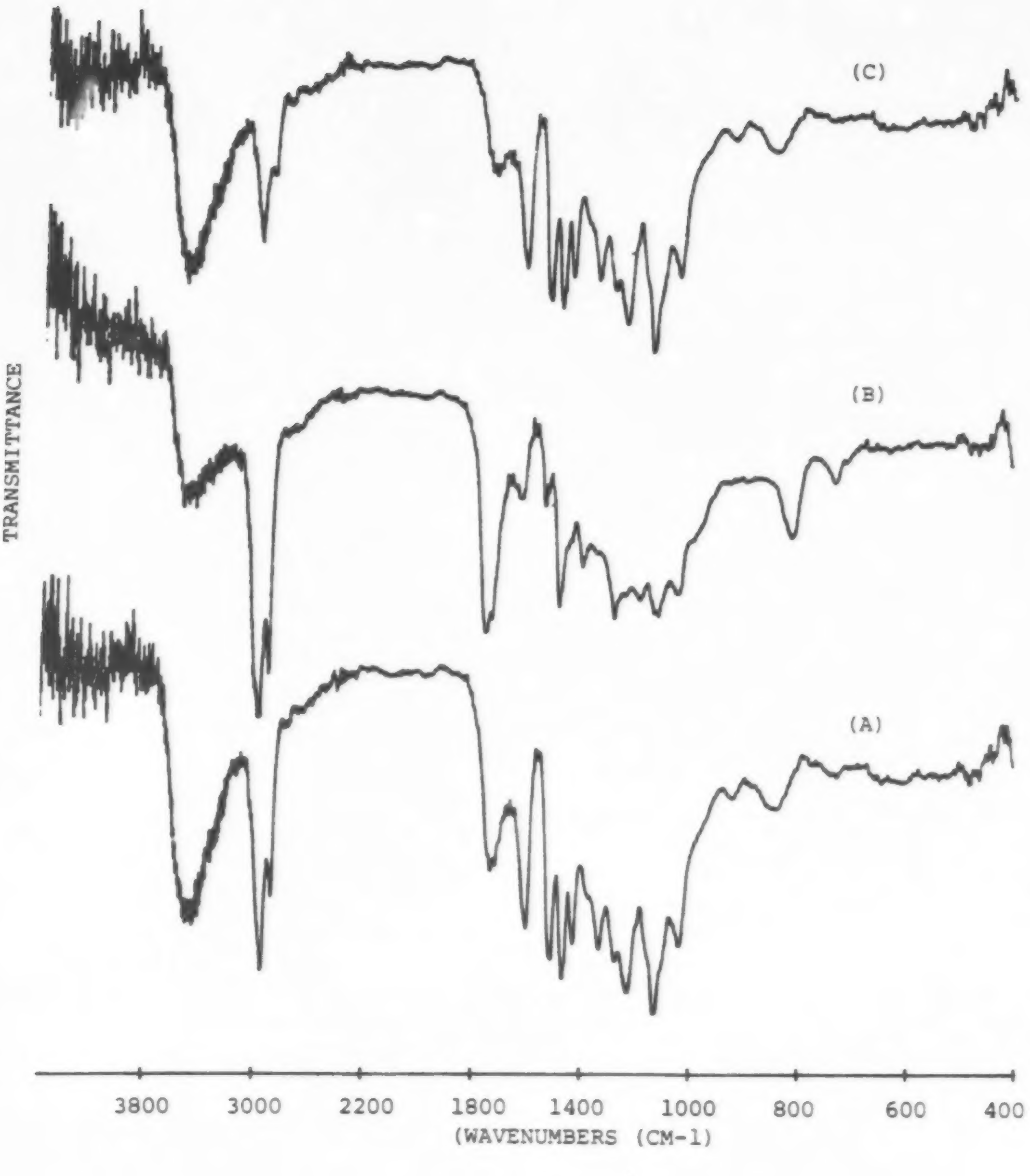

Figure 12 IR Spectra of >100K Lignin-Fraction Recovered in Second Ultrafiltration Experiment. (A) Unextracted, (B) Ethyl Acetate-Solubles, (C) Ethyl Acetate-Insolubles

Table 11

Observed IR Absorption Bands and Assignments for Unfractionated Lignin

Wavenumber	Peak Assignment	
3484, 3410	O-H,	alcohols and phenols
2934, 2836	C-H,	aliphatic CH (CH, CH_2, CH_3)
1737	C=O,	free carbonyl group
1720, 1704	C=O,	conjugated carbonyl
1605, 1515	C=C,	aromatic ring
1458	C-H,	methyl and methylene
1417	C-H,	aromatic ring
1335	C-H,	methyl
1261	C-O,	guaiacyl ring
1220	C-O,	syringyl ring
1120	C-O,	phenol
1031	C-O,	primary alcohols
916, 842	=C-H,	isolated H, aromatic ring
835	=C-H,	2 C-H adjacent H, aromatic ring

The ^{13}C NMR spectra recorded for the unfractionated lignin and the five fractions are shown in Figure 13. Table 12 presents the assignment of signals for the unfractionated lignin based on reports of Lüdemann and Nimz (1975a,b), Reynolds *et al*. (1984), Ralph (1988), and Levy and Nelson (1972). The more informative peaks in the ^{13}C NMR spectrum of the starting material are at 56.5 ppm (OCH_3), 104 ppm (HC=CH, side chain), 115 ppm ($C_{aromatic}$, ortho to C-OH), 148 and 152 ppm ($HO-C_{aromatic}$ and $CH_3-O-\underline{C}_{aromatic}$). The spectrum shows small peaks at 162, 163, 165, and 167 ppm which could be interpreted as carbons (carbonyls) of esters or aromatic acids.

The spectra of the five fractions have differences in the relative intensity of carbon resonances (Table 13). The spectra of the <5K and >100K fractions show narrow peaks in the aliphatic (18-35 ppm) and carbonyl (175) regions. These peaks have a relatively high intensity (due to a short relaxation time) and can be assigned to an aliphatic (fatty) acid. The intensity of phenolic carbon (152-153 ppm) is lower in <5K fraction than in the unfractionated lignin and the intensity increases with increasing molecular weight of the fraction. Because of the nature of the spectra, these intensity differences are probably a measure of the differences in the phenolic content at the free ends of the macromolecular lignin structures.

Examination by GC-MS of the ethyl acetate extracts of the five fractions of lignin indicated the presence of benzoic acid derivatives, fatty acids and possibly some nonpolar dimers (Niemelä 1989; Alén *et al*. 1984; Morita 1972).

The lignin-fractions recovered from the second fractionation run were subjected to nitrobenzene oxidation. These were performed to examine the heterogeneity of the fractions and as a reference point for the oxidation work in Objective B. The results are summarized in Table 14. All the yields obtained were lower than those we had previously obtained from steam-treated aspenwood lignins, except for when an acidic catalyst was used during the

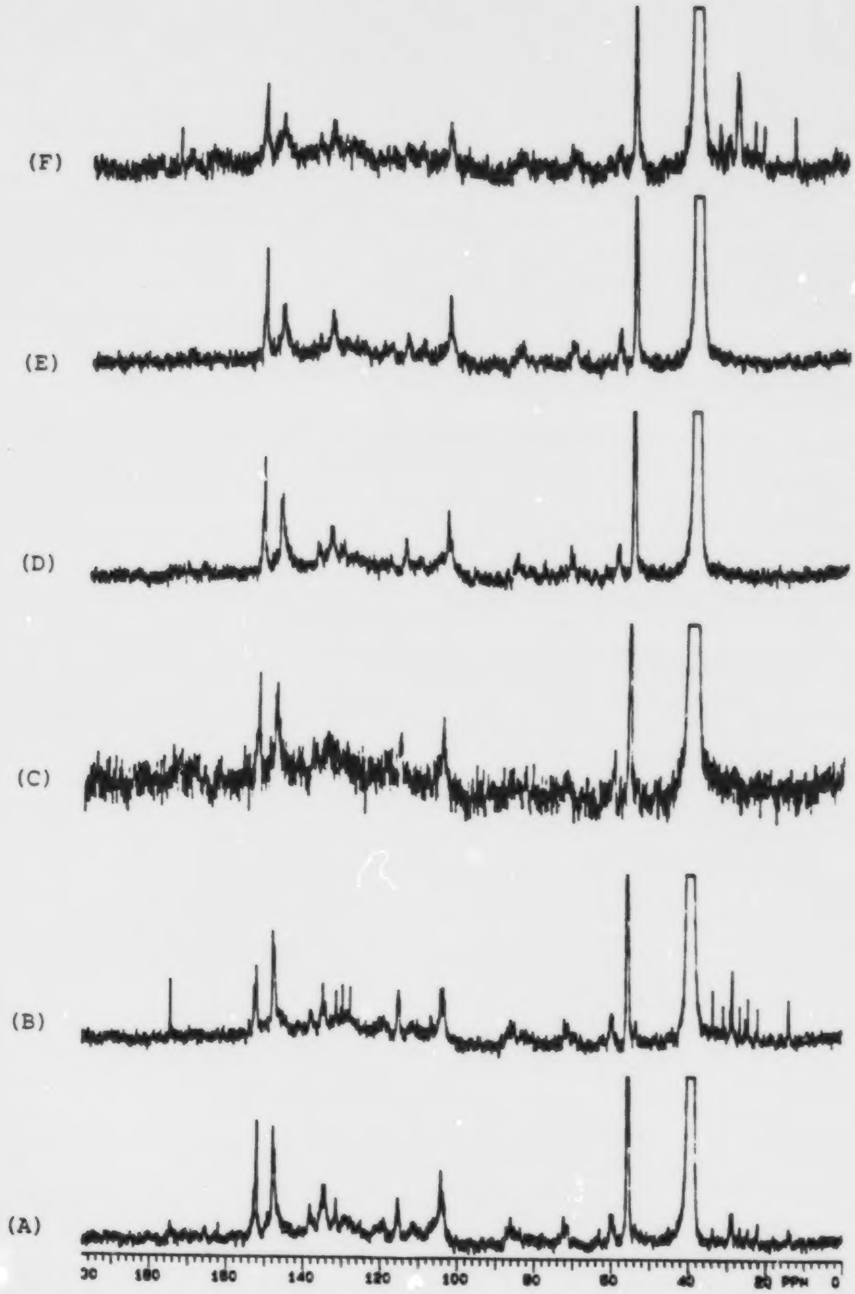

Figure 13 ^{13}C NMR Spectra of Unfractionated Lignin and Lignin-Fractions Isolated By Method 2 in Second Ultrafiltration Experiment. (A) Unfractionated, (B) <5K, (C) 5-10K, (D) 10-30K, (E) 30-100K, (F) >100K

Table 12

Assignments of Signals in the ^{13}C NMR Spectra of Unfractionated Lignin

Signal no.	Chemical shift* (ppm)	Assignment
1	167.0	O=C ester or acid
	162.5	
	162.0	
2	153.4	HO-Caromatic
	152.7	
3	148.5	CH_3O-Caromatic
	147.0	
4	138.2	HCaromatic
	135.7	
	134.9	
	132.0	
	115.9	
5	104.9	C=C
	104.4	
	104.2	
6	88.0	Cside chain Cβ in β-O-4 linkage
	86.6	
	86.0	
	85.0	
	82.0	
7	72.8	Cside chain Cα in β-O-4 linkage
	72.0	
8	60.8	Cside chain Cγ in β-O-4 linkage
	60.0	
	59.5	
9	56.5	Cmethoxyl
10	29.6	Caliphatic, CH2, CH3
	29.0	
	27.5	
	24.0	
	18.0	

* centered value

Table 13

Relative Peak Intensities (%) in ^{13}C NMR Spectra of Unfractionated Lignin and Lignin-Fractions From Second Ultrafiltration Experiment

Lignin	Aliphatic carbon	Methoxyl carbon	$C\alpha, C\beta, C\gamma$	C=C	HCaromatic	C-OH aromatic	C-OCH3 aromatic	C=O (ester or acid)
Unfractionated	5.0	18.1	11.7	11.7	27.0	8.1	17.2	1.2
>100K	14.0	18.9	11.6	8.4	17.0	9.5	16.8	4.0
30-100K	-	16.4	16.3	13.7	19.0	9.5	22.4	2.5
10-30K	-	19.1	14.9	12.8	23.4	8.5	14.9	6.4
5-10K	-	16.9	15.9	9.5	29.6	6.3	15.9	6.0
<5K	8.7	15.2	15.2	8.7	30.4	6.5	13.0	2.1

Table 14

Yields of Products from Nitrobenzene Oxidation of the Lignin-Fractions Obtained in the Second Ultrafiltration Experiment

Sample	Sample Weight (mg)	YIELDS				Ratio
		Ether Ex.(mg)	V[a] (% wt)	S[a] (%wt)	(V + S) (%wt)	S/V
Recovery method 1						
Unfract.	16.8	13.7	3.02	8.39	11.4	2.8
>100 K	22.9	16.5	3.81	6.96	10.8	1.8
30-100 K	25.9	13.1	3.84	8.47	12.3	2.2
10-30 K	20.4	9.3	2.37	6.28	8.6	2.6
5-10 K	11.3	7.5	1.44	4.75	6.2	3.3
<5 K	9.3	6.1	1.45	3.79	5.2	2.6
Recovery method 2						
Unfract.	12.0	9.8	3.38	7.99	11.4	2.4
>100 K	10.4	9.7	3.40	6.99	10.4	2.1
30-100 K	14.0	6.8	4.44	10.1	14.5	2.3
10-30 K	11.8	5.6	2.69	8.19	10.9	3.0
5-10 K	12.2	9.3	2.58	7.52	10.1	2.9
<5 K	11.8	5.3	2.60	7.33	9.9	2.8

[a] V = vanillin, S = syringaldehyde

steam pretreatment. The reason for the lower yields is unclear. For the lignin-fractions from the two precipitation methods, higher yields of aldehydes are obtained from fractions with higher average molecular weights and these also have higher vanillin contents.

3.1.2 Batch UF to Provide Material for Concordia University (Sub-Contract)

From a 20 L fraction of an alkaline extract of steam-treated aspenwood (240°C, 100s), 155.5 g (O.D. wt) of lignin was recovered by acidification, heat treatment and filtration. A further fraction (60L) of the alkaline extract was subjected to ultrafiltration using membranes in the order YM 100, YM 30, and YM 10 to produce four fractions. Precipitation as for the unfractionated extract resulted in the yields shown in Table 15. The total yield of fractions represents 88% of the unfractionated yield.

An examination was made of the supernatant solution from the acid precipitation of the lowest cut-off filter membrane (YM 10) of the large scale run, because of the loss in combined yield of precipitated lignin-fractions experienced in each UF run versus the unfractionated yield.

From the extraction solvent of the supernatant solution, an aliquot (25 mL) yielded 0.51 g (20.4 mg/mL) of solids. Therefore, from the original alkaline extract (60 L), yielding theoretically 466.5 g of unfractionated lignin, 45.5 g of ethyl acetate soluble material was present or 0.1 g organic solubles/(g of precipitated lignin) in the resulting supernatant solution after acidification of the 10K cut-off filtrate. Previously, we have extracted with diethyl ether and ethyl acetate unfractionated alkaline extracts from steam-treated aspenwood (240°C, 80s) and obtained a combined yield of 0.05 g organic solubles/(g of precipitated lignin). These results suggest that a small contribution to the loss in yield of precipitated lignin is low molecular weight material that condenses with higher molecular weight material and

Table 15

Yields of Precipitated Lignin-Fractions in Larger-Scale Ultrafiltration Experiment to Provide Material for Concordia University

Fraction	g (O.D.)
Unfractionated	155.5
>100K	92.5
30-100K	138.2
10-30K	70.8
<10K	106.7[a]
Total	408.2

[a] Estimated yield. Only 2/3 of this extract was precipitated as 1/3 was accidentally contaminated in storage.

therefore is precipitated when unfractionated extracts are acidified.

Analysis by GC/MSD was made of the ethyl acetate extract from the supernatant solution. Not unexpectedly, the dominant component present was p-hydroxybenzoic acid. No attempt was made to identify all the minor components. Quantification by SIM of the p-hydroxybenzoic acid indicated that it was present at a concentration of 4.2 mg/mL in the extract, representing a total yield of 9.8 g from the original alkali extract (60 L). Considering the content of esters of p-hydroxybenzoic acid in aspenwood, the above is not an unreasonable number.

Molecular weight distribution data were determined for the lignin-fractions prepared for Concordia University. The results are summarized in Table 16, and the molecular weight distributions obtained are shown in Figure 14. The curve for the >100K fraction again showed a large portion of lower molecular weight material present, but again this curve is not truly representative because of the fraction of the acetylated lignin not soluble in THF.

3.1.3 Multiple Batch Versus Constant Volume Ultrafiltration

Because of concerns with respect to the distribution of low molecular weight materials in fractions from our original single stage batch ultrafiltrations, filtrations were carried out using the method described by Uloth and Wearing (1989). They dialysed black liquor using 2.3 volumes of fresh water to separate lignin and remove membrane-permeable species from it.

In the first fractionation, the alkaline extracts from the steam-treated aspenwood were subjected to ultrafiltrations. In the second fractionation, an alkaline solution of lignin from which the low molecular weight material had been removed was fractionated. Each lignin-containing solution was subjected to filtration using 100K, 30K, and 10K membranes, using 2.5 times the initial

Table 16

Molecular weight distribution data for the lignin-fractions prepared for Concordia University

Fraction	U.V.		R.I.	
	M_n	M_w	M_n	M_w
Unfract.	677	5425	985	6752
>100K[a]	444	6164	683	7570
30-100K	628	7616	1109	9196
10-30K	427	3721	744	5625
<10K	406	1960	594	3103

[a] material only partially solubilized by acetylation

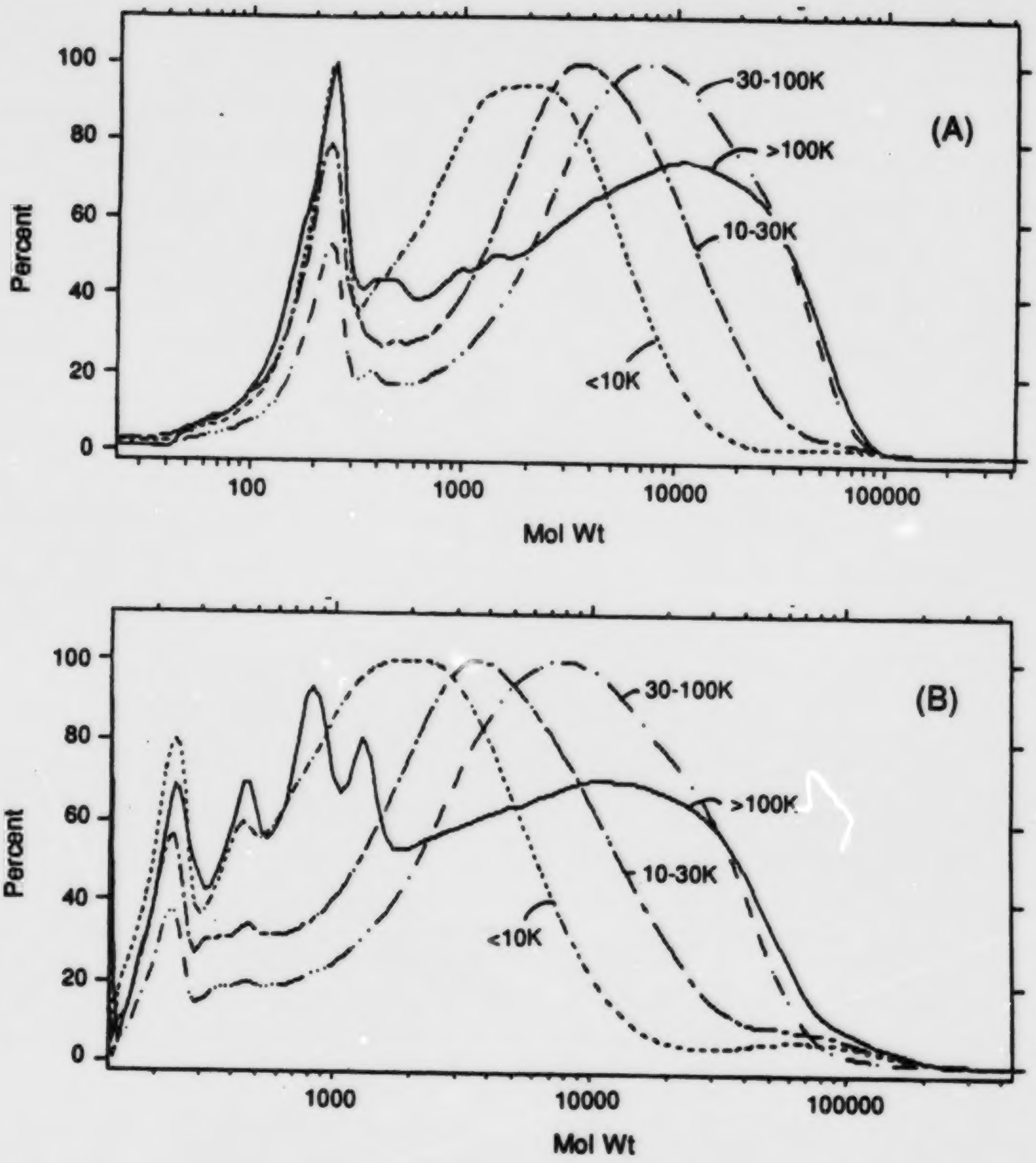

Figure 14 Molecular Weight Distributions (Polystyrene Equivalents) for Lignin-Fractions (>100K, 30-100K, 10-30K, <10K) Recovered in Ultrafiltration to Produce Material for Concordia University. (A) UV detection, (B) RI detection

volume of fresh alkali to achieve the separation and reconcentrating the filtrate after each stage to give comparable starting concentrations of lignin. Fresh alkali, instead of water, was used as the feed solvent because otherwise as the filtration proceeded precipitation of lignin could be a serious problem. Because in the later filtration stages the increasing concentration of hydroxide could be a problem, and because we were comparing essentially a constant volume diafiltration with our original single stage batch ultrafiltration, for further comparison a three batch style filtration, similar to the method of Drouin and Desrochers (1988) for purification of black liquor was also undertaken.

To determine the amount of soluble material present, samples of unfractionated lignin were subjected to Soxhlet extraction with ethyl acetate or diethyl ether. The lignin contained 11.5 % and 1.2 % soluble material, respectively.

The yields of lignin-fractions from constant volume and multiple batch ultrafiltrations are gathered in Table 17 and for the constant volume filtration of the alkaline solution prepared from the ethyl acetate-extracted lignin in Table 18. The yields from the constant volume and multiple batch ultrafiltrations of the alkaline extracts are similar, but not directly comparable with the yields from the fractionation of the ethyl acetate-extracted lignin. The fraction yields are not directly comparable with the original ultrafiltration experiments. The fact that the constant volume and multiple batch ultrafiltrations could not be run using the YM 10 membranes suggests that there is a lignin or alkali concentration dependence to the ultrafiltration. The preparation of the alkaline solution from the ethyl acetate-extracted lignin highlighted one of the problems with the lignin recovery method used. Method 2, which includes heating of the acidified lignin extract, leads to the production of alkali-insoluble material.

To determine if part of the insolubility problem of the ethyl acetate

Table 17

Yields (g O.D.) of Lignin-Fractions from Constant Volume Diafiltration and Multiple Batch Ultrafiltration

Fraction	Constant volume	Batch-wise
>100K	24.2	25.4
30-100K	45.5	41.7
<30K	22.8	24.9
Total	92.5	92.0

Table 18

Yields (g O.D.) of Lignin-Fractions for Experiment Using Constant Volume Diafiltration of Ethyl Acetate-Extracted Lignin

Fraction	Yield		
	(g)	% of original lignin	% of extracted lignin
Original lignin	96.1	-	-
EtOAc Extractives	14.1	15.	-
Extracted lignin	80.0	83.	-
Alkali-insolubles	23.0	24.	29.
>100K	18.7	19.	23.
30-100K	24.9	26.	31.
30K	6.2	7.	8.

extracted lignin arose from the removal of low molecular weight components by the solvent extraction, which may aid in its dissolution, attempts were made to redissolve the ethyl acetate-extracted lignin in alkaline solution with known amounts of phenol added. The results of these tests are given in Table 19. At high levels of phenol addition increased solubility of the lignin was obtained, however, a substantial part was still insoluble. An attempt to perform the same experiment using the ethyl acetate extracted material from the lignin could not be made because these vacuum-dried extracts would not redissolve completely in the alkaline solution.

Molecular weight distribution data were determined for all the lignin-fractions isolated during this experiment and are presented in Table 20. Also included is the percentage of THF-insolubles present after acetylation. Elution volume curves are shown in Figures 15-18. Unfortunately, the high percentages of THF-insoluble material makes interpretation of these data difficult. The original intention of this set of experiments was to determine the source of the lower molecular weight material indicated in the HPSEC chromatograms of the higher molecular weight fractions in the first and second ultrafiltration experiments. From the data presented, we cannot determine the source of the low molecular weight material. Several points merit consideration.

Firstly, two samples of unfractionated lignin were isolated from the alkaline extracts used for this set of experiments. Their molecular weight distributions differ and furthermore differ from those of the unfractionated material isolated for the first two ultrafiltration experiments. This suggests that the isolation of material by method 2 is inconsistent.

Secondly, the quantities of THF-insolubles obtained after acetylation for the fractions from the ethyl acetate-extracted lignin in comparison with the THF-insolubles for the fractions from the constant volume and multiple batch

Table 19

Yields of Insoluble Material from Redissolution of Ethyl Acetate-Extracted Lignin in Alkaline Solution with Added Phenol

Phenol added (% wt of lignin +phenol)	Insoluble precipitate (% wt of lignin + phenol)	Insoluble precipitate (% wt of lignin)
0	29.3	29.3
3.0	26.4	27.2
6.1	26.7	28.4
11.3	16.4	18.5
20.1	13.6	17.1

Table 20

Molecular Weight Distribution Data for the Lignin-Fractions Obtained by Constant Volume and Multiple Batch Ultrafiltration of the Alkaline Extracts and Constant Volume Ultrafiltration of the Alkaline Solution Prepared from Ethyl Acetate-Extracted Lignin[a]

Lignin-Fraction	M_n	M_w	THF-Insolubles (%)
Unfractionated lignin	487 506	3700 4387	5.2 2.6
Constant Volume UF Alkaline Extracts			
>100K	304	1713	45.1
30-100K	312	1849	21.2
<30K	402	1349	17.9
Multiple Batch UF Alkaline Extracts			
>100K	234	683	39.1
30-100K	270	1327	23.2
<30K	389	1544	25.0
EtOAc-Extracted Lignin			
Unfractionated	560	4315	32.8
Alkali-insoluble fraction of EtOAc-Extracted Lignin	231	1063	89.0
Constant Volume UF Alkali-Solubles of EtOAc-Extracted Lignin			
>100K	329	2075	49.9
30-100K	551	4243	2.1
<30K	550	2520	0.6
Underivatized Samples			
EtOAc-Extracted Unfractionated Lignin	598	2354	47.2
EtOAc-Solubles from Lignin Extraction	594	1219	0.3
EtOAc-Extracted Lignin <30K from UF	499	1435	3.4

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[a] Using UV detection

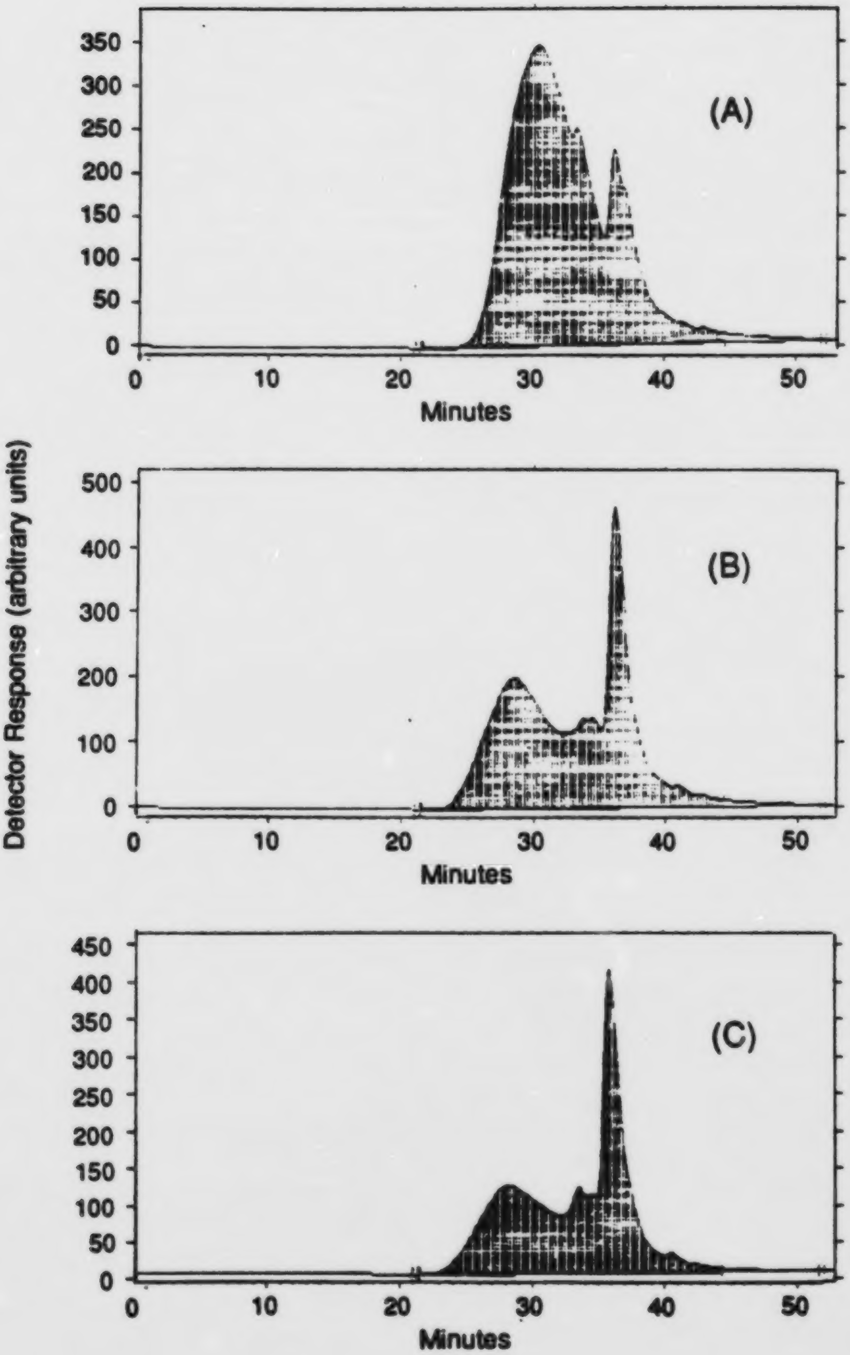

Figure 15 HPSEC Chromatograms for the Acetylated Lignin-Fractions Obtained by Constant Volume Ultrafiltration of the Alkaline Extracts of Steam-Heated Aspenwood Water-Insolubles. (A) <30K, (B) 30-100K, (C) >100K

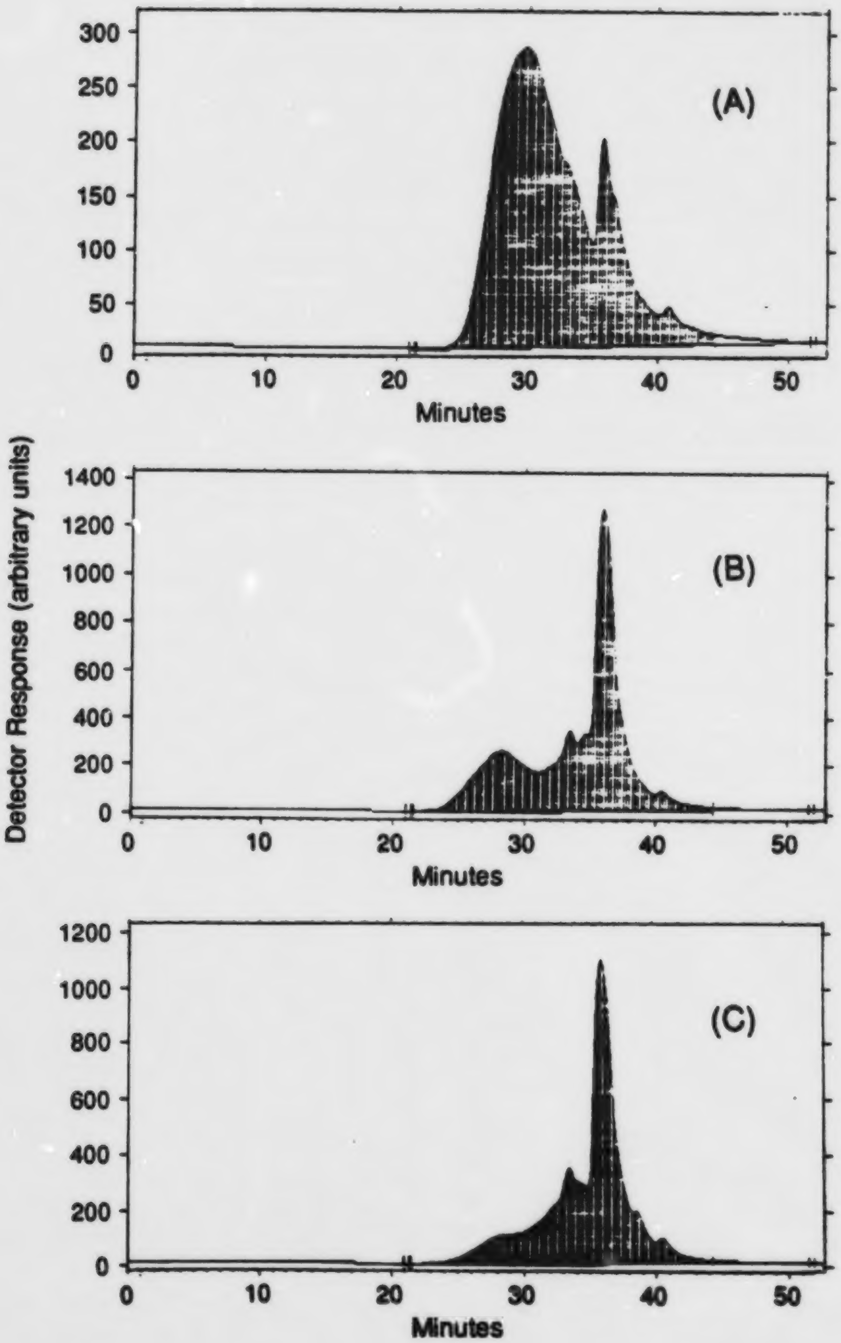

Figure 16 HPSEC Chromatograms for the Acetylated Lignin-Fractions Obtained by Multiple Batch Ultrafiltration of the Alkaline Extracts of Steam-Heated Aspenwood Water-Insolubles. (A) <30K, (B) 30-100K, (C) >100K

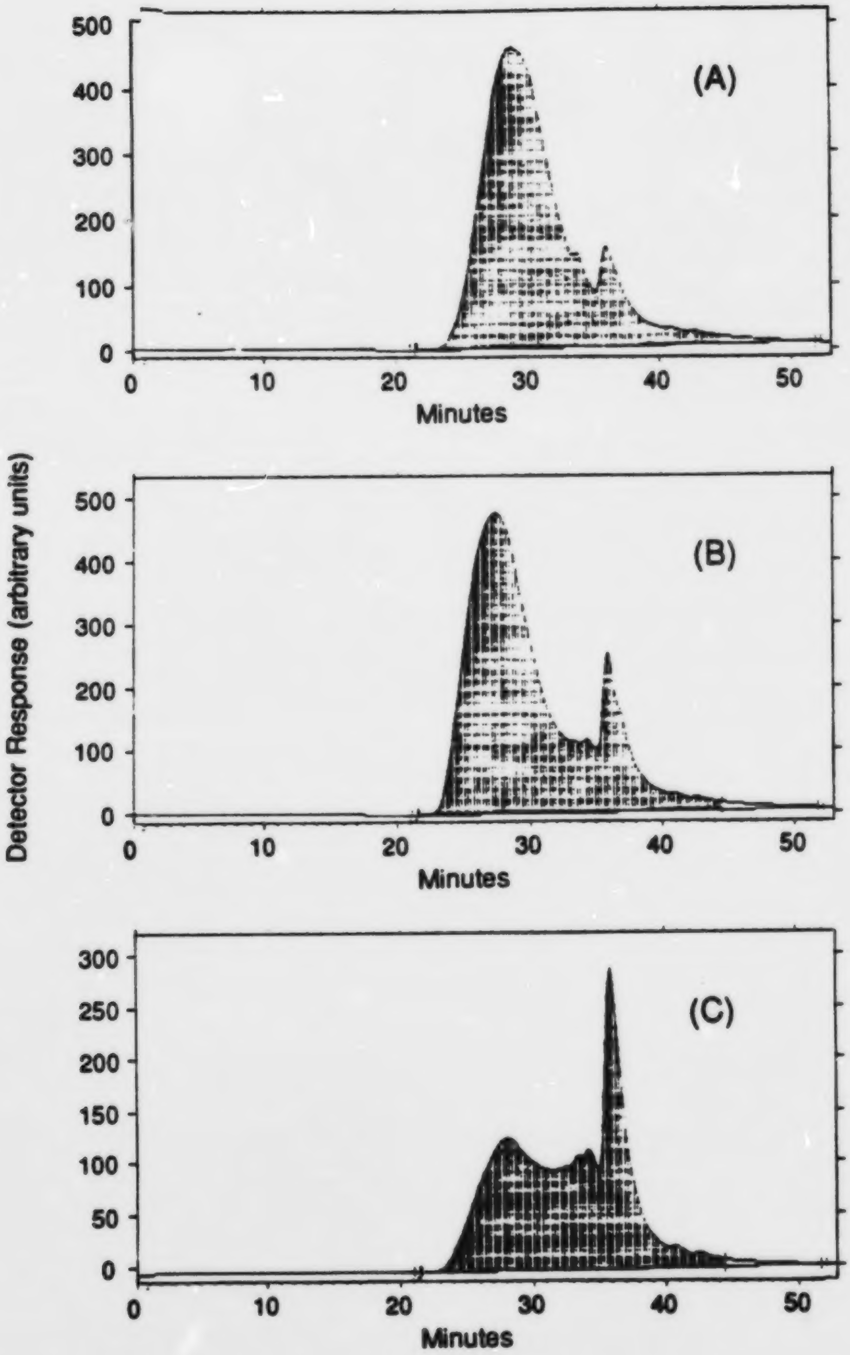

Figure 17 HPSEC Chromatograms for the Acetylated Lignin-Fractions Obtained by Constant Volume Ultrafiltration of the Alkaline Solution Prepared from Ethyl Acetate-Extracted Lignin. (A) <30K, (B) 30-100K, (C) >100K

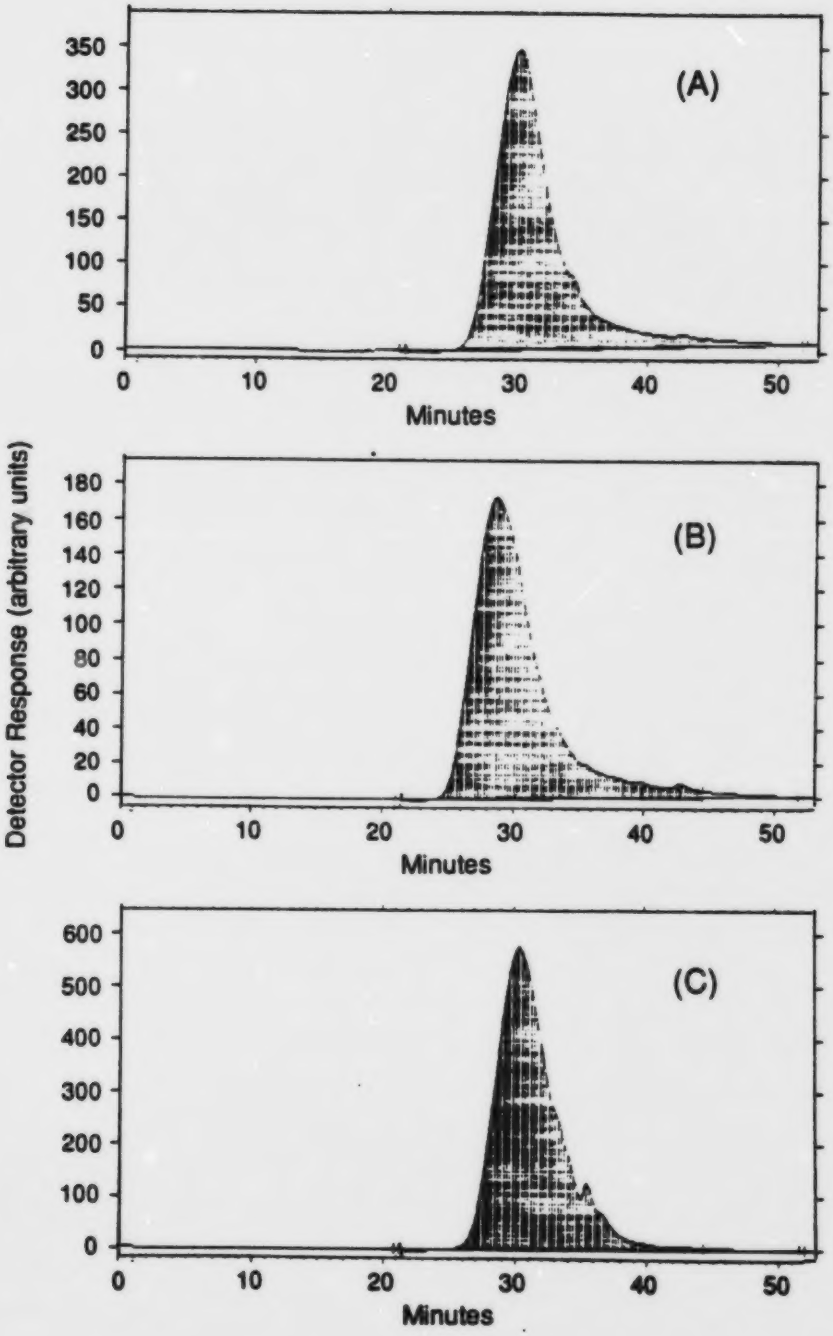

Figure 18 HPSEC Chromatograms for (A) the Unacetylated <30K Lignin-Fraction Obtained by Constant Volume Ultrafiltration of the Alkaline Solution Prepared from Ethyl Acetate-Extracted Lignin, (B) the THF-Soluble Component of the Ethyl Acetate-Extracted Lignin, (C) the Ethyl Acetate-Solubles from the Preparation of the Ethyl Acetate-Extracted Lignin

ultrafiltrations of the alkaline extracts suggest that most repolymerization or condensation of the lignin occurred during the initial recovery process. However, we had not seen this insolubility problem previously, except for the highest molecular weight fractions. This may indicate that there was a problem with the higher salt contents present in these ultrafiltration experiments. Any repolymerization or condensation of the lignin during recovery may also be competing with acidolysis to produce low molecular weight components.

Thirdly, inspection of the elution volume curves for the unacetylated fractions, for example <30K ethyl acetate-extracted lignin fraction (Figure 17) compared to the acetylated material (Figure 18), suggests that there may be an artifact (37-38 min) produced by the derivatization method. This artifact becomes more apparent in the samples with higher levels of THF-insolubility. Whether this in an artifact or not could possibly be tested by using an alternative recovery method for isolation of the acetylated products, for example precipitation of the product by diluting the reaction mixture in water. Unfortunately, this alternative recovery method might lead to loss of molecular weight components.

From the results presented, it appears that the molecular weight distributions and properties of the lignins recovered after ultrafiltration are affected by the recovery process. The fractions obtained by ultrafiltration suggest that it may be inappropriate to fractionate this type of lignin into more than two or three fractions.

3.2 CONVERSION OF LIGNINS TO METHYL ARYL ETHERS, FUELS AND PHENOLIC COMPOUNDS (HIGHER VALUE PRODUCTS) BY ELECTROLYSIS

3.2.1 Characterization of Products of Anodic Oxidation of Lignins

As an approach to low molecular weight chemicals and modified lignins we proposed to study oxidation reactions of steam-treated lignins, particularly by electrochemical methods. From a review of recent literature on electrolysis of lignins (see Section 1.2) our approach was to carry out anodic oxidation of the aspenwood lignin. Our initial plan was to do the electrolyses outlined below in alkaline solution on unfractionated lignin, which has been previously extracted with carbon tetrachloride.

1. Use foametal nickel anode to examine the effects of a range of passage of charge, at room temperature.

2. Compare results obtained with differing anode materials: foametal nickel, glassy carbon, lead dioxide.

3. Examine the use of two anodes at higher temperature (60°C).

4. Compare under one set of conditions the results of electrolysis of unfractionated lignin which has not been extracted with carbon tetrachloride.

5. Use one set of conditions, determined from above experiments, to compare products obtained from electrolysis of high and low average molecular weight lignin-fractions.

6. Compare electrolysis of selected lignins under conditions from above in cell divided by NAFION membrane.

The electrolysis conditions used are similar to those of Yoshiyama *et al.* (1988a) and product isolation is a modification of Utley and Smith (1987) and Bailey and Brooks (1946).

Initially, three experiments (1-3) and a control (C) were run at room temperature using the unfractionated lignin from the first preparation. A foametal nickel (30p, 0.125) anode was used and the total charge passed varied. The product yields are summarized in Table 21. As charge was passed the color of the anolyte changed from black to straw-colored. Attempts were made to see if any change could be followed in the UV spectrum of the anolyte. In each case, a gradual reduction in the intensity of the broad absorbance band at approximately 240 nm was recorded. Under the conditions used, as increased charge is passed the yield of acid precipitable material decreases and the yield of acetone-solubles increases. Infrared spectra recorded of the acid precipitated materials show only small intensity changes in several absorbance bands in the region 1000 - 1700 cm^{-1}. Decrease in the intensity of absorption bands at 1512, 1463 and 1423 cm^{-1} occurs with increased passage of charge, but a marked increase occurs in intensity of the band at approximately 1720 cm^{-1} (Figure 19). Limosin *et al.* (1986) observed similar changes in some lignins electrochemically oxidized in basic aqueous media and ascribed the changes to a decrease in phenyl groups and an increase of the carboxylic groups of the lignins and an opening of benzylic rings.

Electrolyses using three alternative anode materials to foametal nickel (20p, 0.125) were examined. These were foametal nickel (20p, 0.375), glassy carbon (GLCR-10), and lead dioxide (on titanium). The results of these experiments are summarized in Table 21. The glassy carbon electrode was unsatisfactory under the conditions employed and the anolyte was unsuitable for analysis. The lead dioxide anode merits further investigation.

Table 21

Summary of Electrolysis Experiments on Unfractionated Aspenwood Lignin (Carbon Tetrachloride-Extracted) at Room Temperature

Exp. No.	Anode	Applied Voltage (V)	Charge Passed (C)	Sample weight (mg)	YIELDS (mg)			YIELDS (ug) products chloroform-solubles	
					APL[a]	Chloroform -solubles	Acetone-solubles	vanillin	syringaldehyde
C[b]	-	-	-	100	92.	1.3	-	94.4	528.
1	Nickel (30p,0.125)	0.6	827	100	59.	9.0	n.d.[c]	n.d.	n.d.
2	"	0.55	1000	100	33.	5.0	30.3	102.	15.
3	"	0.55	5908	120	19.	9.4	62.1	37.4	5.2
4	Nickel (20p,0.375)	0.50	3574	120	12.	3.0	64.5	tr.[d]	tr.
5	Glassy Carbon	1.5	5107	120	-[e]	-	-	-	-
6	Lead Dioxide	0.8	2133	120	11.	3.8	58.8	64.8	80.8

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[a] APL = acid precipitable lignin

[b] C = control experiment, reprecipitation of lignin (100 mg) from 1M alkali (50 mL)

[c] n.d. = not determined

[d] tr = trace, not quantifiable

[e] Anolyte was contaminated by decomposition of the carbon electrode.

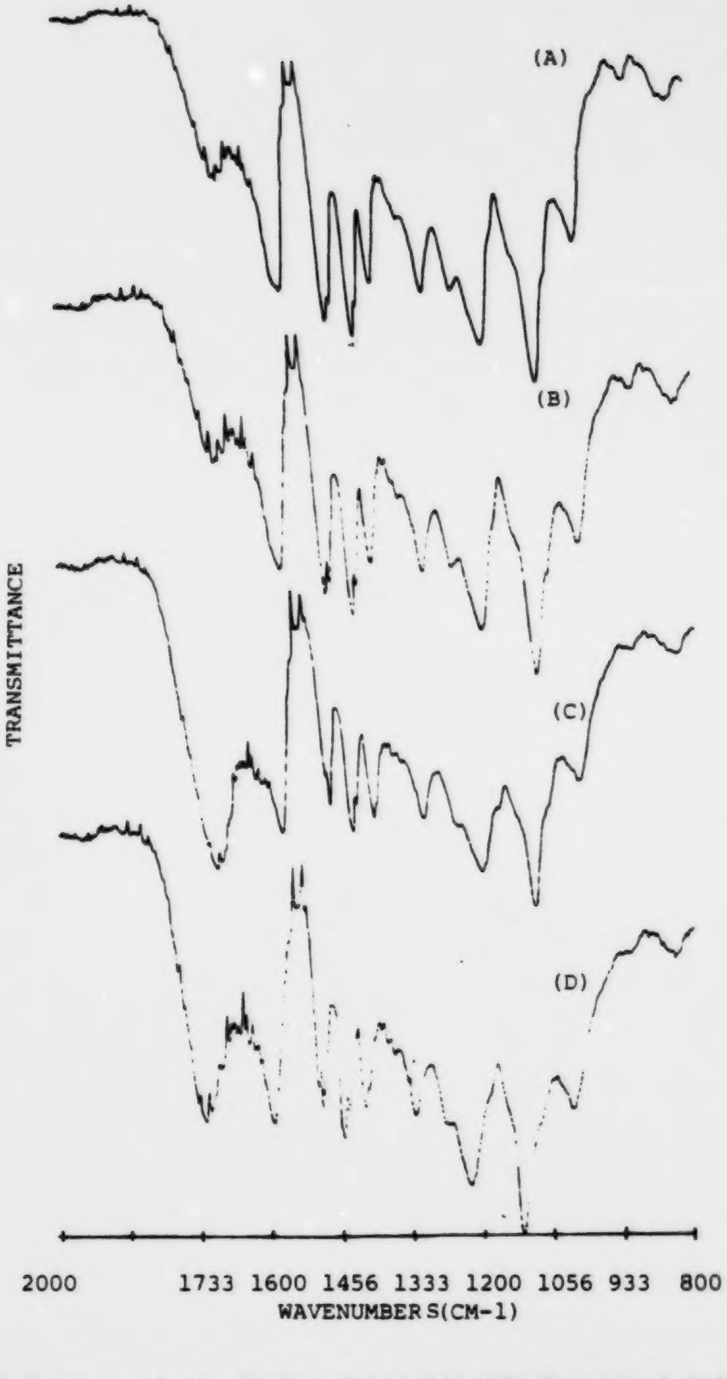


Figure 19 IR Spectra of (A) Carbon Tetrachloride-Extracted Unfractionated Lignin, (B) Control experiment, Reprecipitated Lignin, (C) Acid Precipitated Lignin from Electrochemical Experiment No. 2, (D) Acid Precipitated Lignin from Electrochemical Experiment No. 3

Analysis of the chloroform extracts was started using GC-MSD. In each case, multi-component mixtures are obtained with no obviously dominant products. The extract from the blank experiment contains mainly vanillin and syringaldehyde. These two components were quantified to compare with the extracts from the electrochemical treatments. These results are also presented in Table 21. The highest combined yield of vanillin and syringaldehyde is present in the chloroform extract of the control, but even in the control these products only account for less than 1% of the starting lignin. This suggests that the low molecular weight products produced by oxidation may be undergoing reaction in the systems examined. Under the conditions of anodic degradation of lignins that Yoshiyama *et al.* (1989) studied they suggested that the initially formed degradation products are further oxidized to carbon dioxide. Further work to identify other products in the chloroform extracts is necessary.

The results of further electrochemical experiments (7-12) are summarized in Table 22. Experiments 7,9-11 were run to examine the effects of carrying out the electrolysis at higher temperature (60°C) using a lead dioxide anode. In experiment 12, a foametal nickel anode was used for comparison. Experiment 8, was run using a lead dioxide anode at 60°C in an undivided cell to determine whether there were any effects caused by having the cell divided. Additionally, this experiment was run at twice the scale to compare the effectiveness of extracting the reaction mixture after acidification with chloroform and ethyl acetate.

Operating at higher temperature reduced the electrolysis time substantially by allowing usage of higher current density. As observed previously for the foametal nickel anode at room temperature, with increasing passage of charge the yield of acid precipitable lignin (APL) decreased and the yield of acetone-solubles increased, but there was little variation in the yield of chloroform-soluble material, see Figure 20. The use of ethyl acetate in place

Table 22

Summary of Electrolysis Experiments on Unfractionated Aspenwood Lignin (Carbon Tetrachloride-Extracted) at 60°C Temperature

Exp. No.	Anode	Applied Voltage (V)	Charge Passed (C)	Sample weight (mg)	YIELDS (mg) APL[a]	Chloroform solubles	Acetone solubles
7	Lead Dioxide	0.65	5110	120	19.	2.4	61.3
8[b]	"	0.45	800	240	61.(61)[c]	3.1(10.2)	63.1(32.3)
9	"	0.65	10450	120	0.5	1.5	110.7
10	"	0.65	1100	120	60.	3.8	56.7
11	"	0.5	3355	120	21.	6.1	90.0
12	Nickel 30p,0.125	0.5	1955	120	3.	1.0	113.2

[a] APL = acid precipitable lignin

[b] Experiment at twice scale using undivided cell

[c] Yields in parentheses for material recovered using ethyl acetate in place of chloroform

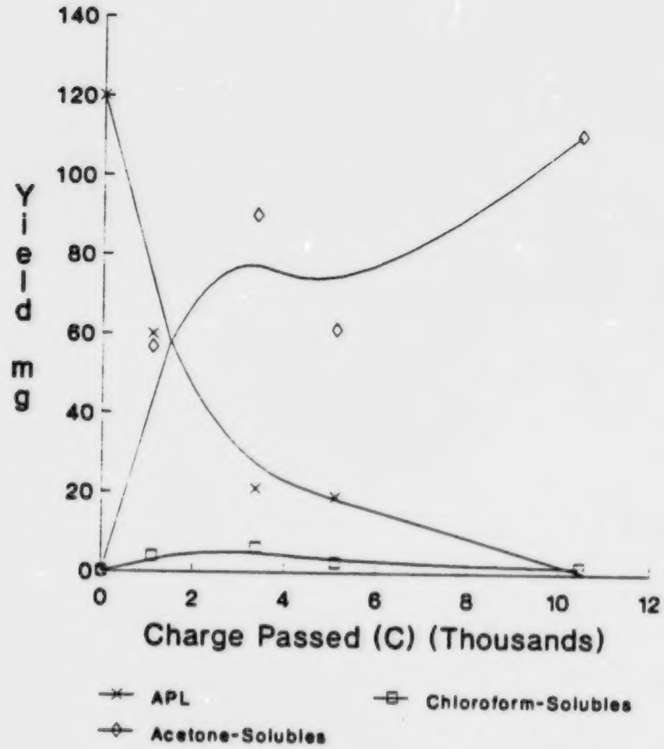


Figure 20 Yields of Recovered Products as a Function of Charge Passed

of chloroform after acidification and removal of the APL, gave a higher yield of soluble material. Preliminary analysis by GC suggests that there is little difference in the monomeric composition of these fractions.

The use of a nickel electrode at 60°C appears to lead to a more rapid degradation of the starting material to acetone-solubles.

The highest (>100K MWCO) and lowest molecular weight (<5K MWCO) fractions from the second fractionation were electrolyzed using a lead dioxide anode at 60°C. The results of these experiments are summarized in Table 23 with results obtained previously for electrolysis under similar conditions of unfractionated lignin.

In the electrolysis of the low molecular weight fraction there was a rapid drop in the measured current and therefore the electrolysis was stopped after limited passage of charge. Product yield over 100% was obtained. The reason for this is presently unclear. The low molecular weight fraction gave a very high yield of chloroform soluble product. The volatile products in these fractions are yet to be determined.

A sample of the unfractionated lignin was electrolyzed in an electrolysis cell divided using a #901 NAFION membrane. Only a low applied voltage could be used with this cell and only a low passage of current was achieved. The result of this experiment is summarized in Table 24 with results obtained previously for electrolysis of the same lignin sample using the cell divided with the porous frit. A product yield of over 100% was obtained. The reason for this is presently unclear. In this initial experiment with the membrane divided cell, a low yield of acid precipitable lignin was obtained at low passage of current at a low applied voltage.

Characterization of acetone-soluble electrolysis products was made. The

Table 23

Summary of Electrolysis Experiments on Fractionated Aspenwood Lignin at 60°C

Exp. No.	Anode	Applied Voltage (V)	Charge Passed (C)	Sample weight (mg)	YIELDS (mg) APL[a]	Chloroform solubles	Acetone solubles
Fraction >100K							
13	Lead Dioxide	0.55	3000	120	41.	4.2	56.7
Fraction <5K							
14	"	0.55	1120	120	8.	91.	53.
Unfractionated							
10	Lead Dioxide	0.65	1100	120	60.	3.8	56.7
11	"	0.5	3355	120	21.	6.1	90.0

[a] APL = acid precipitable lignin

Table 24

Summary of Electrolysis Experiments on Aspenwood Lignin at 60°C Using Membrane Cell Divider

Exp. No.	Anode	Applied Voltage (V)	Charge Passed (C)	Sample weight (mg)	YIELDS (mg)		
					APL[a]	Chloroform solubles	Acetone solubles
NAFION MEMBRANE							
15	Lead Dioxide	0.45	710	120	39.	16.7	84.1
FRITTED CELL							
10	Lead Dioxide	0.65	1100	120	60.	3.8	56.7

[a] APL = acid precipitable lignin

infrared spectra recorded of the acetone recovered materials show marked changes from the starting lignin, see for example Figure 21 for the material recovered from electrolysis runs 3 and 12. There is a general loss of distinct absorbance bands in the 1000-1400 cm^{-1} range but an increase in the 1700-1800 cm^{-1} range. This could indicate the formation of quinoid-type structures or carbonyls, for example, in esters.

^{13}C NMR spectra were recorded for the acetone-soluble materials recovered from electrolysis experiments 3 and 12 (Figure 22). The spectra of both materials are characterized by sharp spectral features suggesting that the material is substantially depolymerized from the starting lignin. This supports the results obtained by HPSEC for these materials, see below. In the spectra, there are substantial loss in peak intensity for methoxyl carbon and considerable loss of aromatic carbon resonances. In both spectra, there are new resonances with high intensity in the regions around 30 ppm and 158-162 ppm. The resonances at about 30 ppm suggest production of aliphatic carbons, and those at 158-162 ppm carbonyl carbons. It is not clear whether the latter arise from carbonyl carbons in esters, anhydrides or lactones, or to quinoidal carbonyls. From literature values for compounds relating to these possible structures an assignment could not be made. Recently, Shchukin and Babkin (1989) suggested that in the electrochemical oxidation of the guaiacyl moiety of lignin o- and p-quinones are intermediates that are further oxidized and ring opened to give dicarboxylic acids. From the work of Shchukin and Babkin (1989) and Limosin *et al.* (1986), the loss of aromatic rings and formation of ring-opened products is more probable.

The molecular weight distribution data obtained for the acetone-soluble products, together with the data for the <5K and 5-10K fractions for comparison are gathered in Table 25. The data for these products were determined without acetylation because of their complete solubility in THF. The results suggest that the acetone-soluble lignin product is substantially

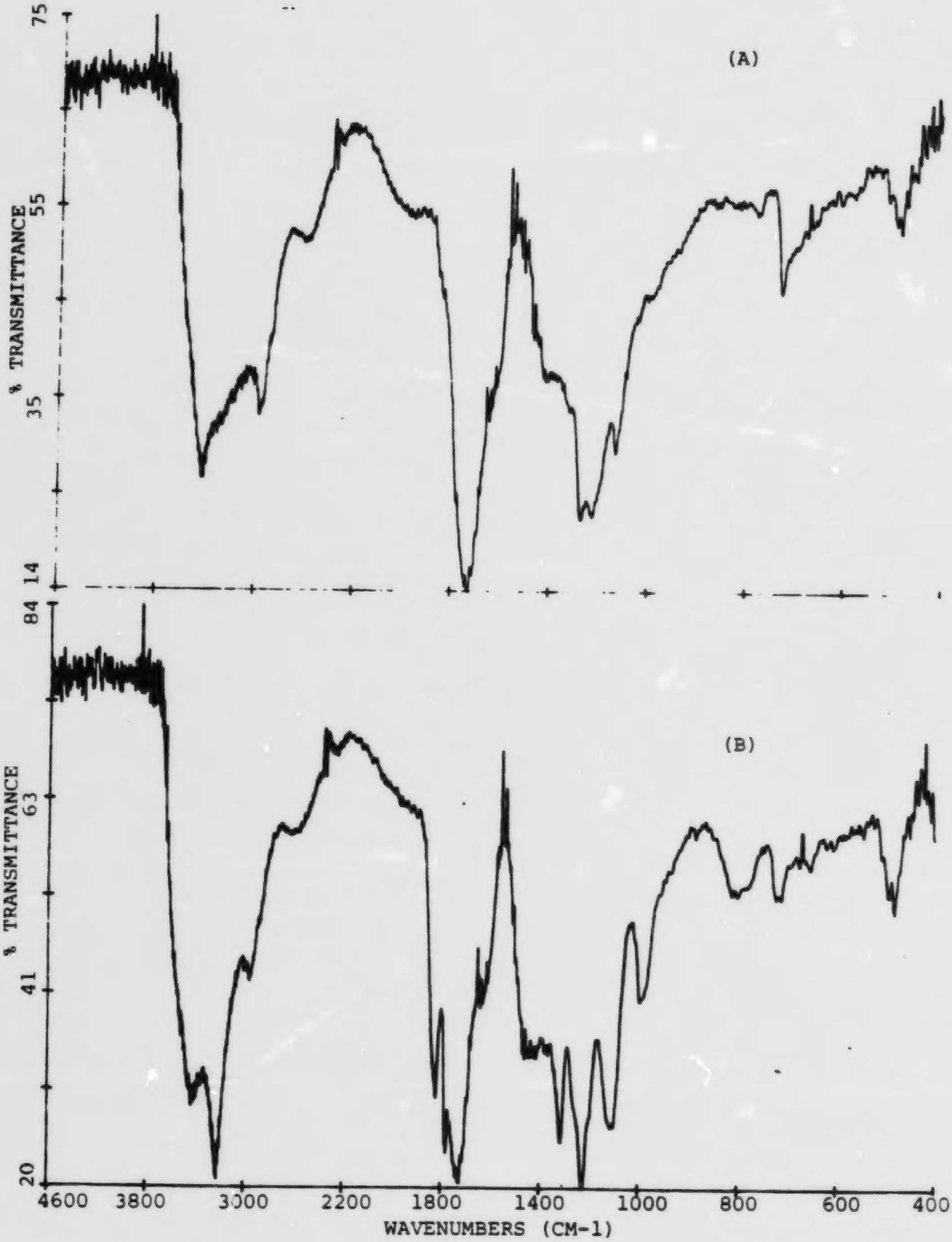


Figure 21 **IR Spectra of Acetone-Extracted Material. (A) Electrochemical Experiment No. 3, (B) Experiment No. 12**

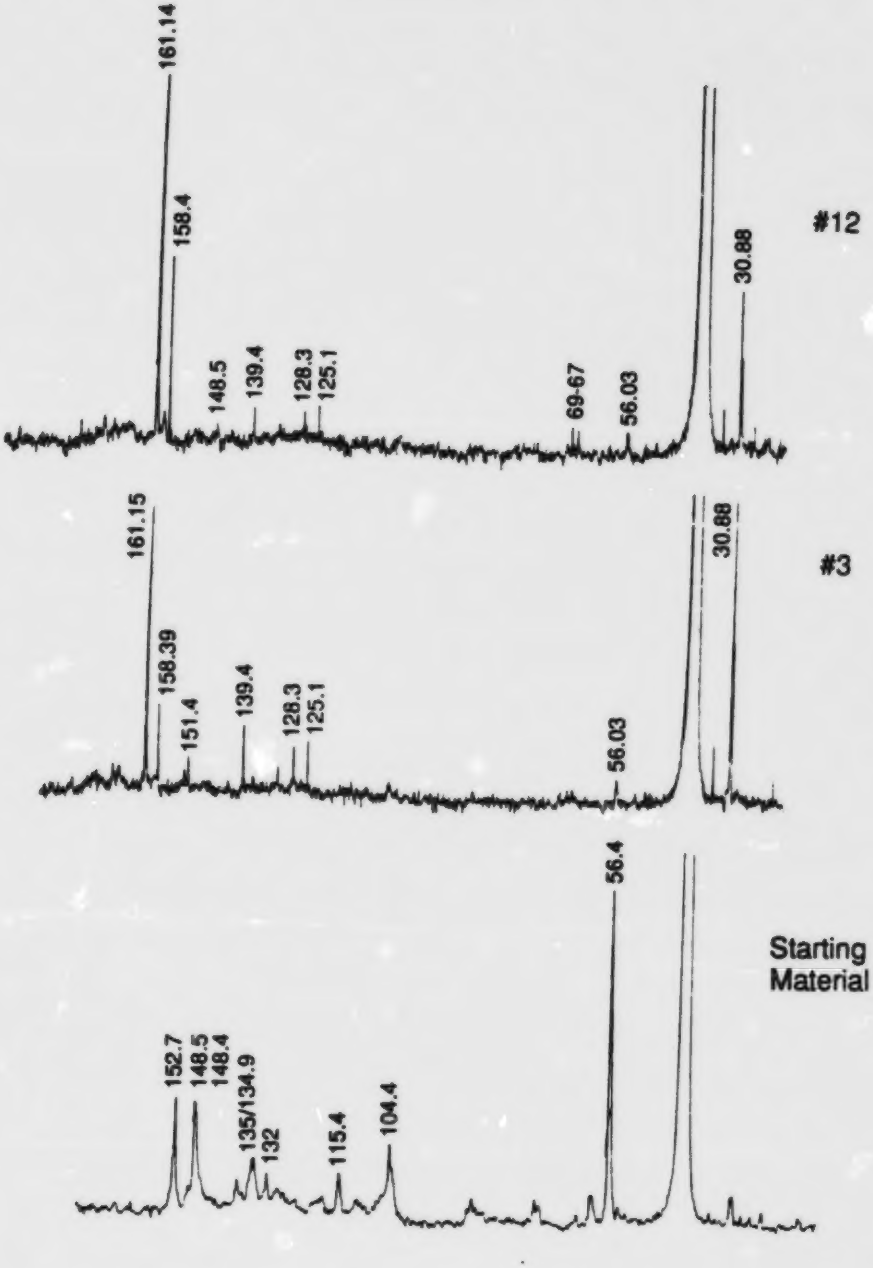


Figure 22 ^{13}C NMR spectra of Acetone-Soluble Products from Electrolysis Experiments No. 3 and 12

Table 25

Molecular Weight Distribution Data for Acetone-Soluble Products Recovered after Electrolysis of Lignin (Unacetylated)

Sample Electrolysis Expt. No.	U.V.		R.I.	
	M_n	M_w	M_n	M_w
2	310	661	309	833
3	269	864	279	2442
4	218	999	248	2147
6	280	1591	291	1720
7	209	618	284	885
8[a]	230[b]	909	294	2192
	200[c]	876	263	1496
9	370	876	350	884
10[a]	266	606	319	1005
11	213	707	339	752
12	309	675	319	1075
13 (>100K Fn)[a]	234	676	312	740
14 (<5K Fn)	348	770	364	738
15 (NAFION membrane)	268	680	329	624
Fn <5K				
Unacetylated	681	1349	621	1911
Acetylated	373	1227	736	2179
Fn 5-10K				
Unacetylated	879	1965	818	2396
Acetylated	391	1856	836	3220
Unfractionated				
Acetylated	559	5275	867	6350

[a] Sample contained very small fraction of material insoluble in THF

[b] Sample recovered after chloroform extraction

[c] Sample recovered after ethyl acetate extraction

depolymerized from the original starting material.

3.2.2 Investigation of the Parameters Important in the Electrolysis of Lignin

To gain an understanding of the parameters important in the electrolysis of lignin to low molecular weight products, a factorial analysis approach was attempted. Parameters to be studied were (low and high value in parentheses): electrolyte concentration (1 M, 3M NaOH), lignin concentration (0.1 g, 1.0 g in anolyte), charge passed (1000 Coulombs, 10000 Coulombs), reaction temperature (25°C, 70°C), and atmosphere (air or nitrogen). The fixed conditions were to be: a fritted H-type cell, platinum cathode, applied potential (v. SCE) 0.5 V, three types of anode material to be studied, lead dioxide, nickel and platinum, and the anode compartment to be stirred. This approach was not successsful. The experiments are described below because they raise a number of issues that should be considered if this approach is tried on similar systems.

Initially, using a lead dioxide on titanium anode, runs S1-S3 were made using the conditions of the first experiment for the parametric analysis ([NaOH], 1 M; Lignin, 1 g; Charge, 10000 C; Temp., 70°C; Atmos., Nitrogen). A number of problems were experienced. In run S1 the gas flow was used to agitate the solution because in the thermostated baths consistent stirring of the anolyte in the electrolysis cell could not be obtained. Bleed through of the dark colored alkaline lignin solution into the catholyte was observed. Previously, this has not been seen in any of the electrolysis runs. This was found to result from the pressure of blowing nitrogen into the cell and also by inspection of the cells due to attack on the frit dividing the cell by the alkaline solution. Condensation in the gas exit line also occurred. The run was stopped after the passage of 3000 C.

Run S2 was then undertaken using modifications in the gas exit line. In this experiment after 20 h only 2976 C of charge had been passed and the electrolysis had essentially stopped (0.005 A approx. 2.5 min/C), (Figure 23). Again some bleed through of anolyte into the catholyte had occurred. When the nitrogen gas inlet was removed the liquid levels in the compartments equalized. On inspection it was discovered that the cell dividing frit had disintegrated. From the electrolyzed starting material (1.003 g, M.C. 3%) were obtained precipitated lignin (0.604 g) and ethyl acetate extract (0.046 g).

Because of the collapse of the cell frit in run S2 it was repeated. Again under the conditions used only 3300 C of charge were passed. With the new fritted cell only very slight leakage into the catholyte was observed. The anolyte was worked up to yield precipitated lignin 0.565 g and ethyl acetate extract 0.039 g. In runs S1-3 no measurement of gas absorption by the ascerite or charcoal traps could be made because of condensation problems. For subsequent runs to circumvent this problem a trap filled with anhydrous calcium chloride trap was placed in line between the condenser and the charcoal filled gas absorbent tube.

Because of the problems being experienced it was decided to try an experiment run S4 under the conditions of experiment 2 of the factorial design. The conditions were as follows: [NaOH], 3 M; Lignin, 1 g; Charge, 1000 C; Temp., 25°C; Atmos., Air.

An immediate problem was that at the originally planned applied potential no passage of charge would occur. The applied working voltage was therefore increased to 0.8 V vs. SCE to get a reasonable initial current. This lead to a smooth electrolysis run, see Figure 24. The weight increases obtained in the ascerite and charcoal traps were 0.021g and -0.001g, respectively. The yield of precipitated lignin was 1.065 g and of ethyl acetate extracts 0.021g. On inspection of the precipitated lignin it appeared to contain salt from

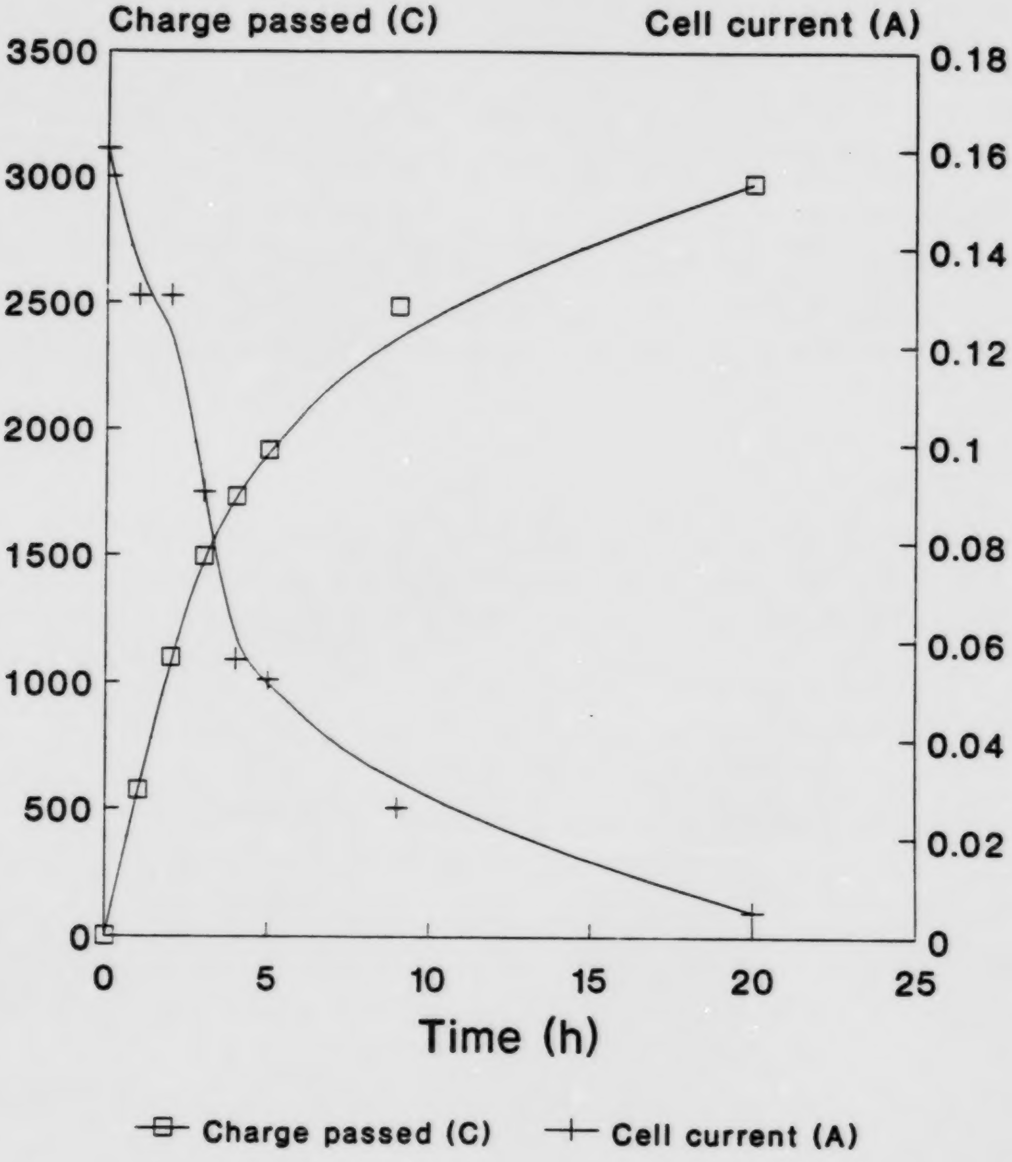


Figure 23 Total Charge Passed and Observed Current versus Duration of Electrolysis for Run S2

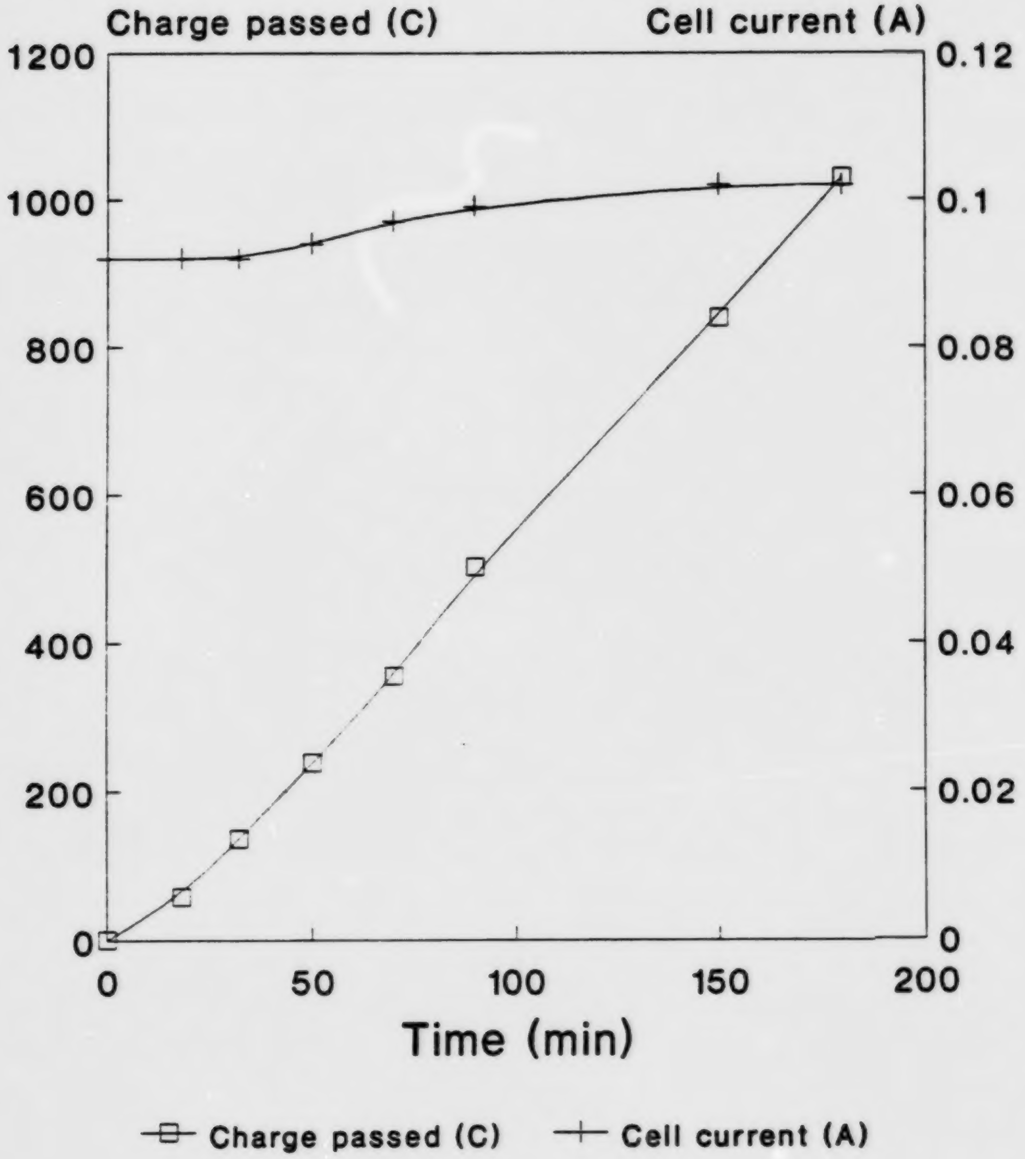


Figure 24 Total Charge Passed and Observed Current versus Duration of Electrolysis for Run S4

precipitation. This could be corrected for by elemental analysis.

From the experience with run S4, it was clear that the selected operating conditions for the parameter investigation were inappropriate. Current vs. potential curves for the different conditions to be investigated were generated (see Section 2.6.4 and Appendix 4.2). An applied working potential of 0.8 V vs. SCE was adopted for the next runs. This is close to the potential which will lead to competing solvent electrolysis but appeared as a realistic potential to conduct these experiments and to compare the parameters agreed upon for this study.

Four experiments were run (S5-8) using the lead dioxide anode with an applied voltage of 0.8 V vs. SCE. These runs are described below and the results of them collected in Table 26.

In run S5 the conditions of experiment one were used: [NaOH], 1 M; lignin 1.0 g; Temp., 70°C; Atmos., Nitrogen; Charge 10000 C. The electrolysis cell compartments were filled initially with alkali in the ratio Cathode:Anode:Reference, 35:60:10. During the run, bleed-through of the dark anolyte into the other cell compartments was observed. The run was stopped after passing only 5500 C of charge because of the low cell current (Figure 25). After removing the gas traps the levels in the cell compartments equalized. The solutions were of reddish brown coloration in comparison to the original black alkaline solution of lignin. By marking the cells prior to removing the gas traps it was determined that during the run the cathode and anode compartments contained approximately 43 and 52 mLs of solution, respectively. Acid precipitable materials were recovered from the anolyte, and the combined catholyte and reference solution, and the resulting supernatant solutions extracted with ethyl acetate. The yields of materials recovered (wt % of original lignin) are given in Table 26. In this and subsequent experiments the acid-soluble lignin-derived material retained in

Table 26

Yields of Products Obtained from Electrolysis Runs Using Lead Dioxide Anode for Attempted Parametric Analysis

	Yield (wt % of starting material)			
	S5	S8	S6	S7
Experimental parameters[a]	1	1	2	2
Starting lignin (g OD)	0.973	0.974	0.975	0.972
Charge passed (c)	5500	7465	620	1000
Organic volatiles (charcoal trap)	0.2	-1.0	-0.2	-1.0
CO_2 trap	0.6	2.6	1.3	2.2
Ppt from anolyte	41.7	48.0[b]	90.4	130.4[c]
Ppt from catholyte + reference cell	8.8	--	0.1	1.8
EtOAc extract anolyte after acid ppt	3.7	7.6[d]	2.5	2.2
EtOAc extract catholyte + reference cells after acid ppt	3.7	--	0.5	.5
Total of recovery	58.7	57.2	94.6	--

---

[a] Experimental parameters:
Set 1: [NaOH], 1 M; Lignin, 1.0 g; Temp., 70°C; Atmos., Nitrogen; Charge, 10000 C; Applied potential 0.8 V vs. SCE.
Set 2: [NaOH], 3 M; Lignin, 1.0 g; Charge, 1000 C; Temp., 25°C; Atmos., Air; Applied potential 0.8 V vs. SCE.

[b] Precipitate from combined cell contents because of disintegration of frits

[c] By inspection precipitate contaminated with salt from precipitation

[d] Extract from combined cell contents because of disintegration of frits

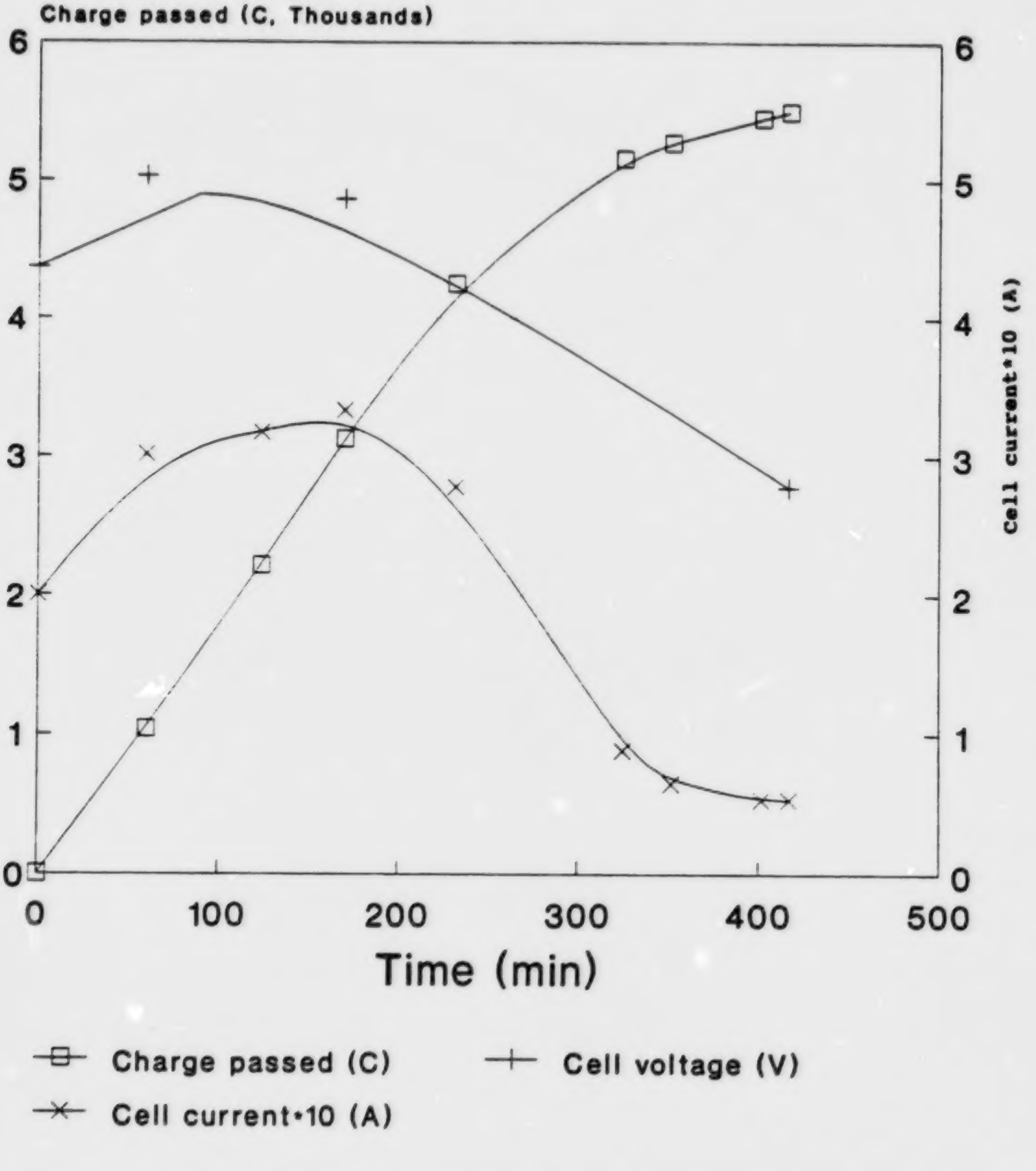


Figure 25 Total Charge Passed, Observed Current and Cell Voltage versus Duration of Electrolysis for Run S5

the supernatant solutions after extraction with ethyl acetate were not determined.

Run S6 used conditions of experimental two of the parametric analysis, using the conditions: [NaOH], 3 M; lignin 1.0 g; Temp., 25°C; Atmos., Air; Charge 1000 C. A smaller inlet gas flow was used to see if this would avoid some of the over-pressure and bleed-through problems experienced. The electrolysis cell compartments were filled initially with the alkaline solution in the ratio Cathode:Anode:Reference, 35:65:10. Bleed through of the dark anolyte into the cathode compartment was observed during the run. The run was stopped after passing only 620 C of charge because of the low cell current (Figure 26). The anolyte was of black coloration and the catholyte was pale yellow. Acid precipitable materials were recovered from the anolyte and catholyte and the resulting supernatant solutions extracted with ethyl acetate.

Because we were concerned with the rate at which we were able to pass current under the experimental conditions adopted for these experiments we repeated this run using the same conditions (S7). Again very slight leakage of the anolyte into the catholyte occurred during the run which was stopped after passage of 1000 C of charge Figure 27. From its appearance the precipitate from the anolyte was contaminated with salt.

In runs S6 and S7, bleed-through and therefore changing cell solution volumes appeared to have been overcome, therefore run 5 was repeated (S8). The electrolysis cell compartments were filled initially with alkaline solution in the ratio Cathode:Anode:Reference, 35:65:10. During the run the solutions in all the cells became rosy-brown in coloration. After stopping the run because of the low cell current at 7465 C (Figure 28), it was determined that all the cell frits had disintegrated, again. The resulting solution was filtered and acidifed to recover acid precipitable products, and the filtrate was extracted with ethyl acetate.

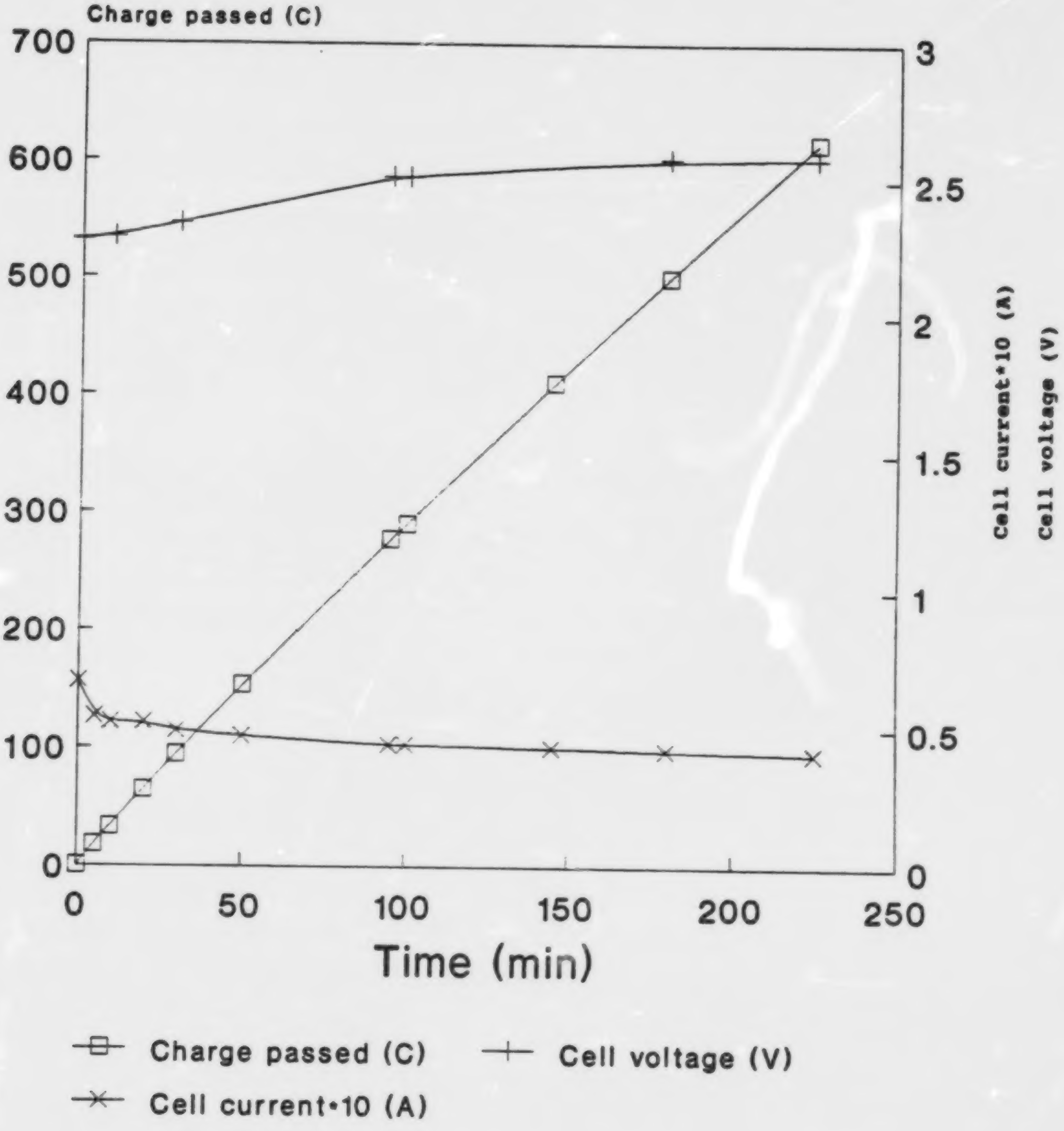


Figure 26 Total Charge Passed, Observed Current and Cell Voltage versus Duration of Electrolysis for Run S6

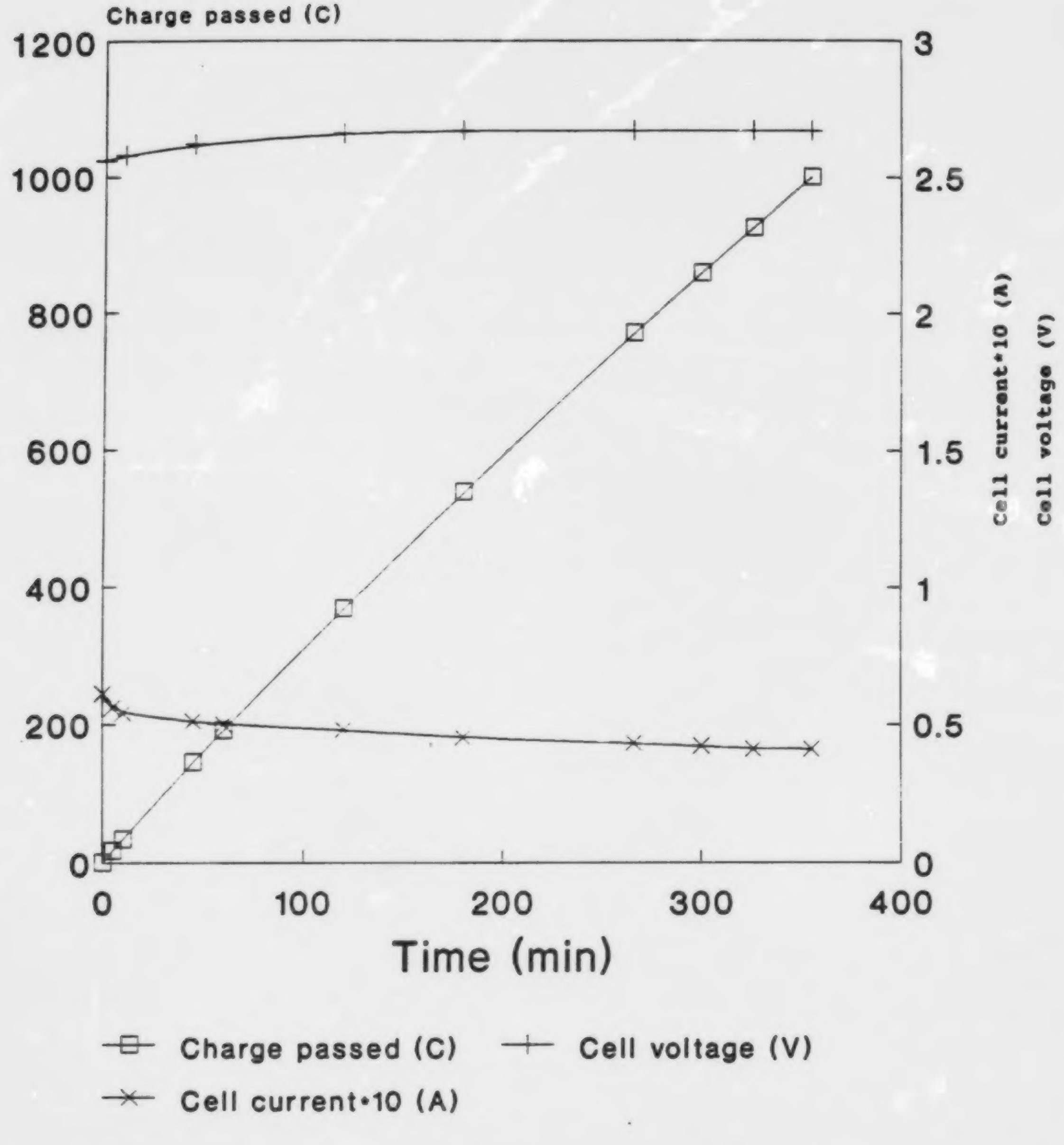


Figure 27 Total Charge Passed, Observed Current and Cell Voltage versus Duration of Electrolysis for Run S7

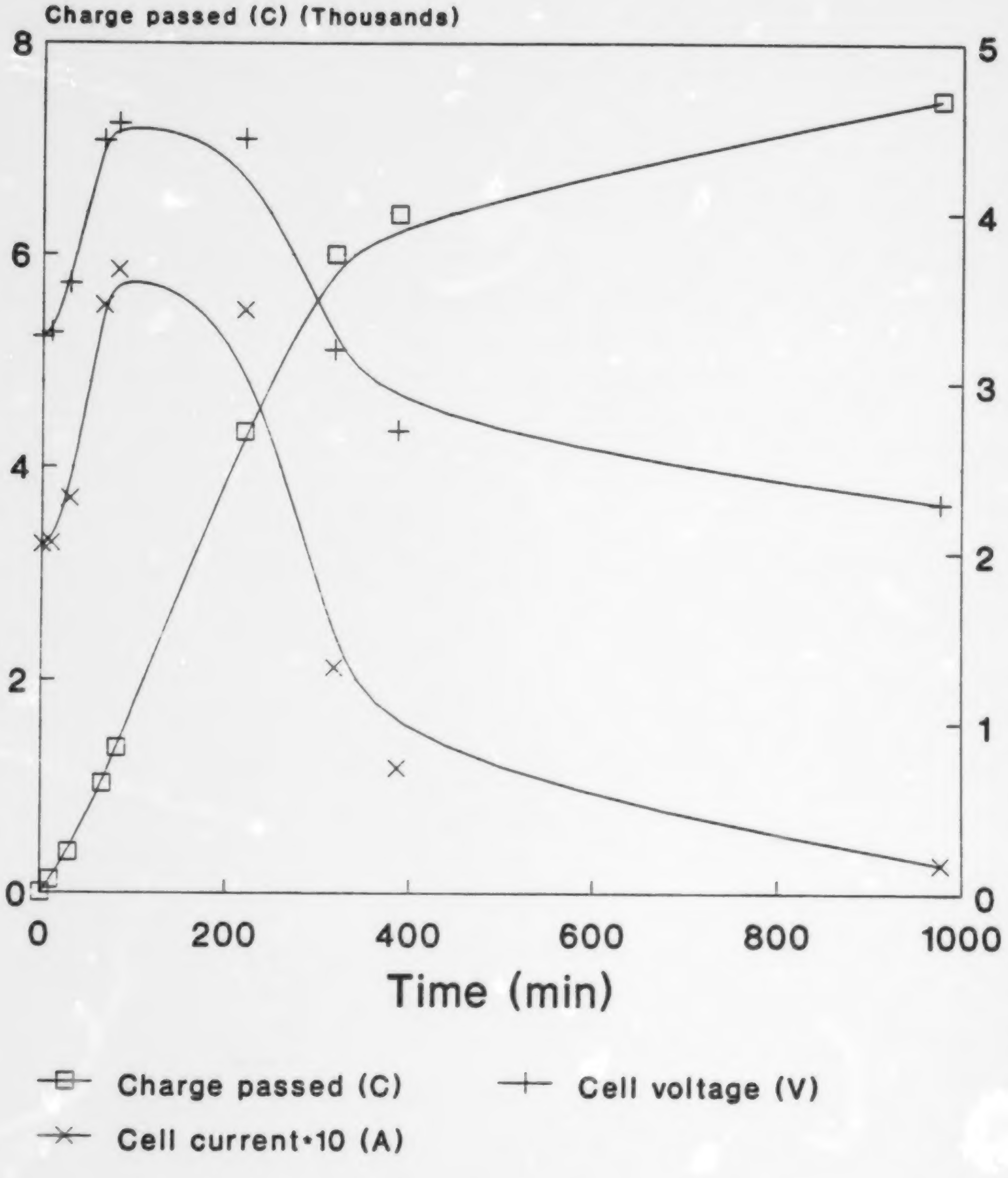


Figure 28 Total Charge Passed, Observed Current and Cell Voltage versus Duration of Electrolysis for Run S8

In runs S5-S8 described above several experimental difficulties were apparent. The over-pressure on the anolytic solution, resulting from the gas absorption traps, led to problems of changing cell solution volumes which affect any quantitative measurements. Additionally, the over-pressure in combination with the temperature and alkali concentration used led to weakening of the cell frits. The above experiments indicate little production of volatile organic products and limited carbon dioxide production. In three of the runs the charcoal traps lost up to the equivalent of 2.5 % of the weight of the absorbant. The entrapment of salt in the precipitated material on acidification appears to be a problem particularly from the 3 M sodium hydroxide reaction mixture.

The operating conditions of the other anode materials to be used were screened to determine if it would be possible to generate the data for the statistical analysis of operating parameters in these systems. As previously for the lead dioxide anode, a series of experiments were undertaken to determine current vs. potential curves for the different conditions to be investigated for both the platinum and foametal nickel anodes. Plots of current versus applied potential were made, see Appendix 4.2. The graphs of applied potential versus cell current for the Foamnickel anode (Figure 29) show one of the difficulties with the selection of parameters for experiments for the factorial analysis. For example, in 1M NaOH at 25°C, an applied potential of 0.6 V gives only a very low initial cell current which with the drop of cell current with time at constant potential, makes experimental runs with high passage of cahrge impossible to perform. In contrast, an applied potential of 0.6 V under the conditions of 1M or 3M NaOH at 70°C is impossible to run because, apart from the severe gassing in the electrolytic solutions, these conditions could result in the potentiostat becoming overloaded. These results suggested it was impossible to perform the parametric analysis as conceived.

In spite of the above concerns five further runs were attempted: to determine

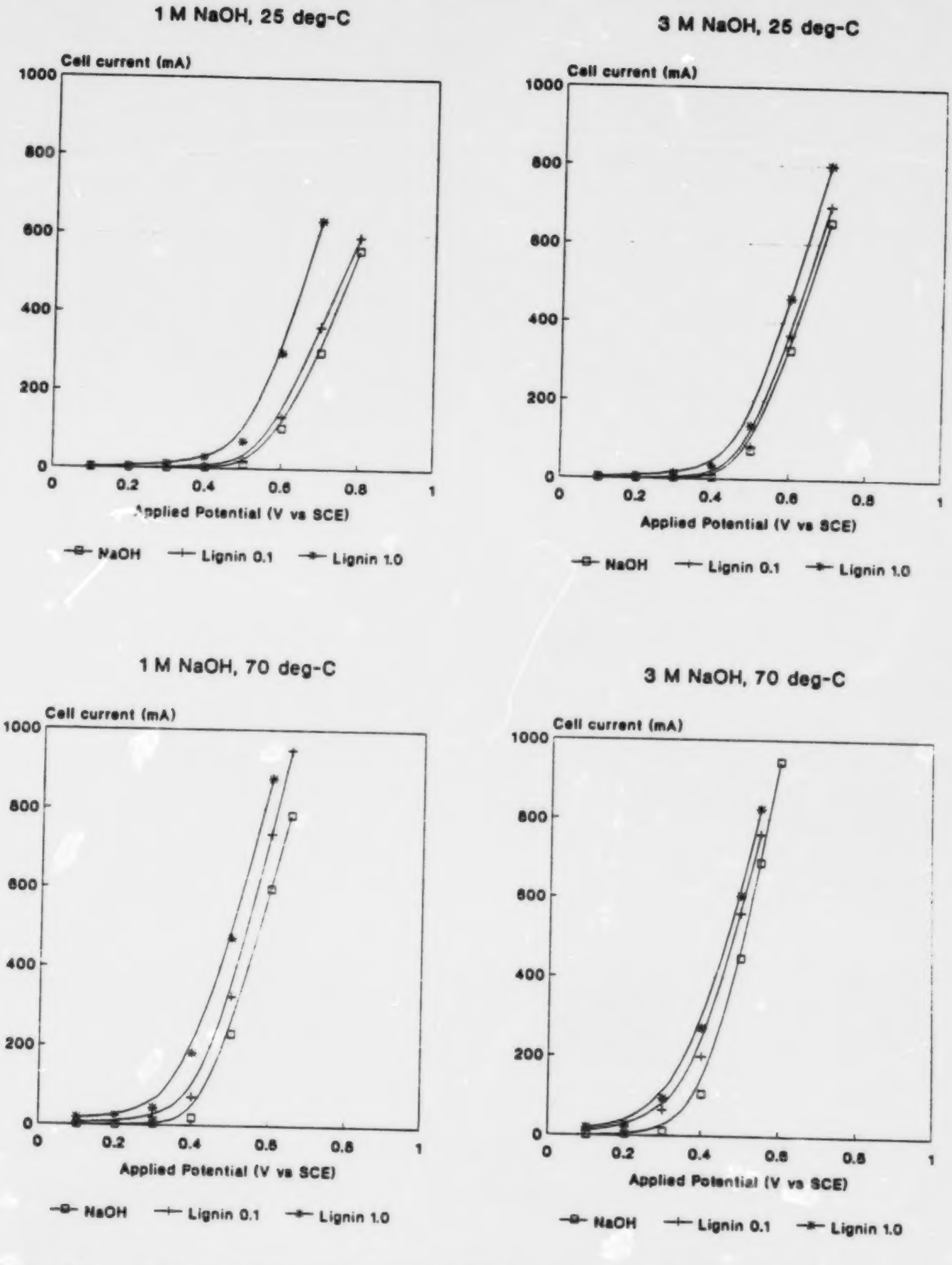


Figure 29 Applied Potential Versus Cell Current for Foamnickel Electrode

how the nickel electrode material would behave; to generate samples to develop the analysis of the alkaline reaction mixture; and to determine the types of products that are being produced under these conditions. Because of the difficulties in runs S5-S8 and the minor production of the gases under the extremes of parameters used for these experiments, the following runs were made using only a carbon dioxide trap, or no gas traps and only sweeping the cells with the desired gas. For acidification hydrochloric acid was used to facilitate washing of the salt formed in the precipitation out of the precipitated material.

The foamnickel anode (30 pore, 2%) with an applied voltage of 0.55 V vs. SCE was used in runs S9-S13 described below. The product yields are given in Table 27. Run 9 used the conditions of experiment one: [NaOH], 1 M; lignin 1.0 g; Temp., 70°C; Atmos., Nitrogen; Charge 10000 C. The electrolysis cell compartments were filled initially with alkali in the ratio Cathode:Anode:Reference, 25:75:8. A charcoal trap was omitted from the cell exhaust line to see if this would alleviate some of the back pressure problems. During the run bleed through of the dark anolyte into the other cell compartments was observed. The run was stopped after passing only 5250 C of charge because of the leakage and the low cell current (Figure 30). After removing the gas traps the levels in the cell compartments equalized. The solutions were of reddish brown coloration in comparison to the black coloration of the original alkaline solution of lignin. Samples were taken from the anolyte and catholyte + reference cell solutions for use in analytical development. Acid precipitable materials were recovered by acidification with hydrochloric acid from the anolyte, and the combined catholyte and reference solution, and the resulting supernatant solutions extracted with ethyl acetate. In these runs the yields of acid soluble-lignin derived materials remaining in the supernatant solutions after extraction with ethyl acetate were not determined.

Table 27

Yields of Products Obtained from Electrolysis Runs Using Foamnickel Anode for Attempted Parametric Analysis

	Yield (wt % of starting material)				
	S9	S10	S11	S12	S13
Experimental parameters[a]	1	1	1[b]	1	2
Starting lignin (g OD)	0.975	0.974	0.977	0.977	0.974
Charge passed (c)	5250	5025	5590	5000	503
CO_2 trap	1.3	--[c]	--	--	--
Ppt from anolyte	52.7	36.6	68.9	40.1[d]	89.6[d]
Ppt from catholyte + reference cell	11.3	11.7	4.5	--	--
EtOAc extract anolyte after acid ppt	4.7	4.7	5.1	4.9	2.7
EtOAc extract catholyte + reference cells after acid ppt	0.7	1.2	0.3	--	--
Total of recovery	70.7	54.2	78.8	45.0	92.3

[a] Experimental parameters:
Set 1: [NaOH], 1 M; Lignin, 1.0 g; Temp., 70°C; Atmos., Nitrogen; Charge, 10000 C; Applied potential 0.55 V vs. SCE.
Set 2: [NaOH], 3 M; Lignin, 1.0 g; Charge, 1000 C; Temp., 25°C; Atmos., Air; Applied potential 0.55 V vs. SCE.

[b] Atmosphere air

[c] No gas traps used

[d] Undivided cell

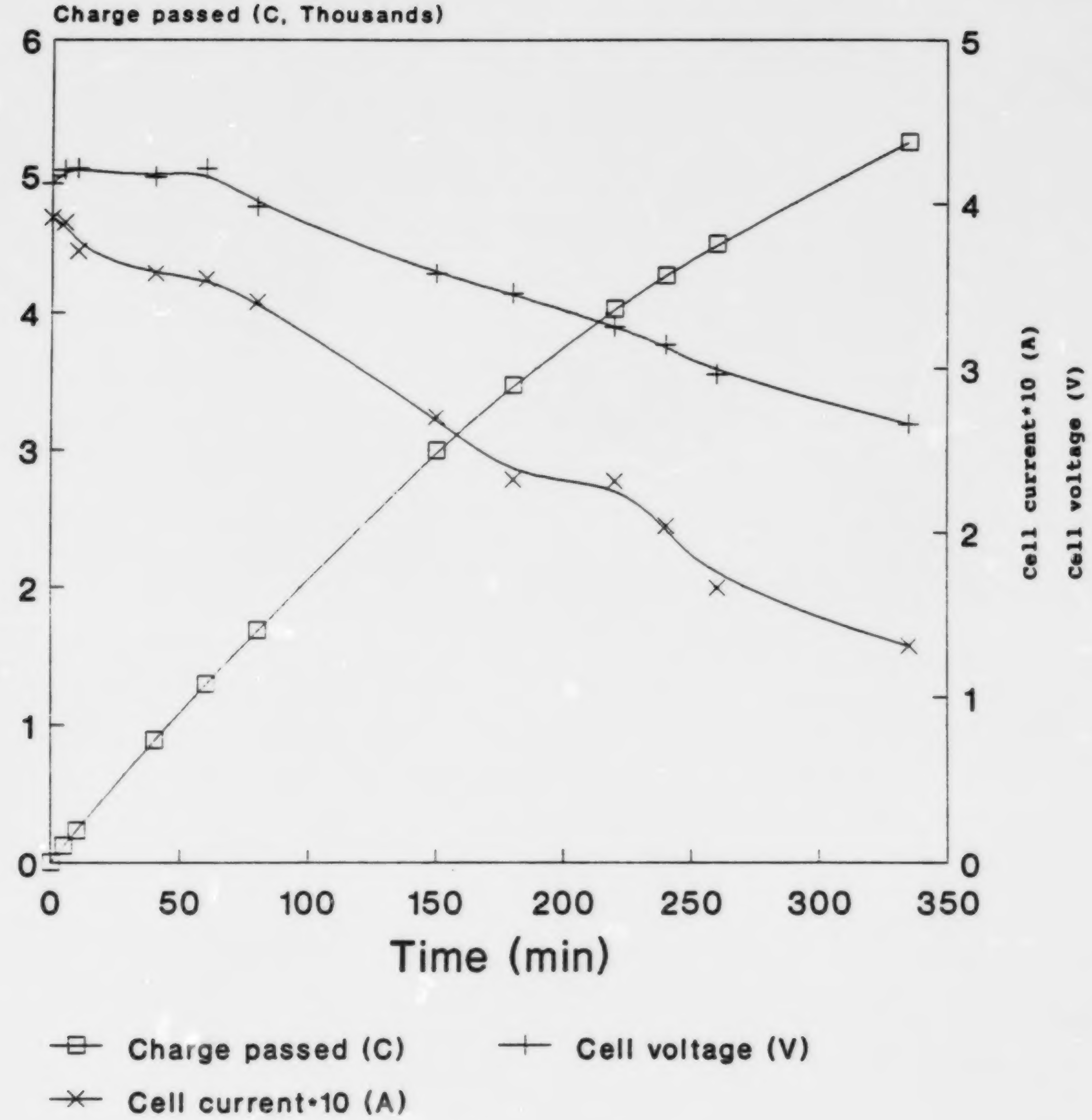


Figure 30 Total Charge Passed, Observed Current and Cell Voltage versus Duration of Electrolysis for Run S9

Run S10 was a repeat of run S9, using the same conditions but without any gas traps to avoid all back pressures on the cell. Bleed through of solution from the anolyte to catholyte compartment still occurred. The run was stopped at 5025 C passed (Figure 31). Run S11 was run under the same conditions as run S10 but with air replacing nitrogen as the gas being passed through the cell to determine whether the presence of oxygen had an effect. Slight bleed through of solution from the anolyte to catholyte compartment occurred. The run was stopped after 5590 C were passed (Figure 32). In run S12 the same conditions as in run S10 were used but an undivided cell was employed. This was because of the suggestion of Fry (1989) that in oxidation systems using a platinum cathode in most cases an undivided cell can be used. The run was stopped after 5000 C were passed (Figure 33). The solution had a dark reddish brown coloration. Run S13 used the undivided cell under the conditions of the parametric analysis of experiment 2. An applied potential was used of 0.55 V as in the above experiments, but unfortunately after only 503 C of charge were passed, the electrolysis equipment experienced power overload and the run was curtailed. The materials were recovered for analysis.

In the above electrolysis runs difficulties were experienced. These related to problems due to the changing levels of solutions in the cells, which affect any attempts at quantitative measurements. In part this may be due to the combination of temperature and alkali concentration attacking and affecting the cell frits.

These experiments were terminated because of the difficulties related to the choice of parameters for the experimental design and the resulting lack of progress to the collection of the information originally intended as the goal of the parametric factorial analysis.

Analysis of the products present in the alkaline solutions and ethyl acetate extracts was attempted to determine whether the electrolytic approach

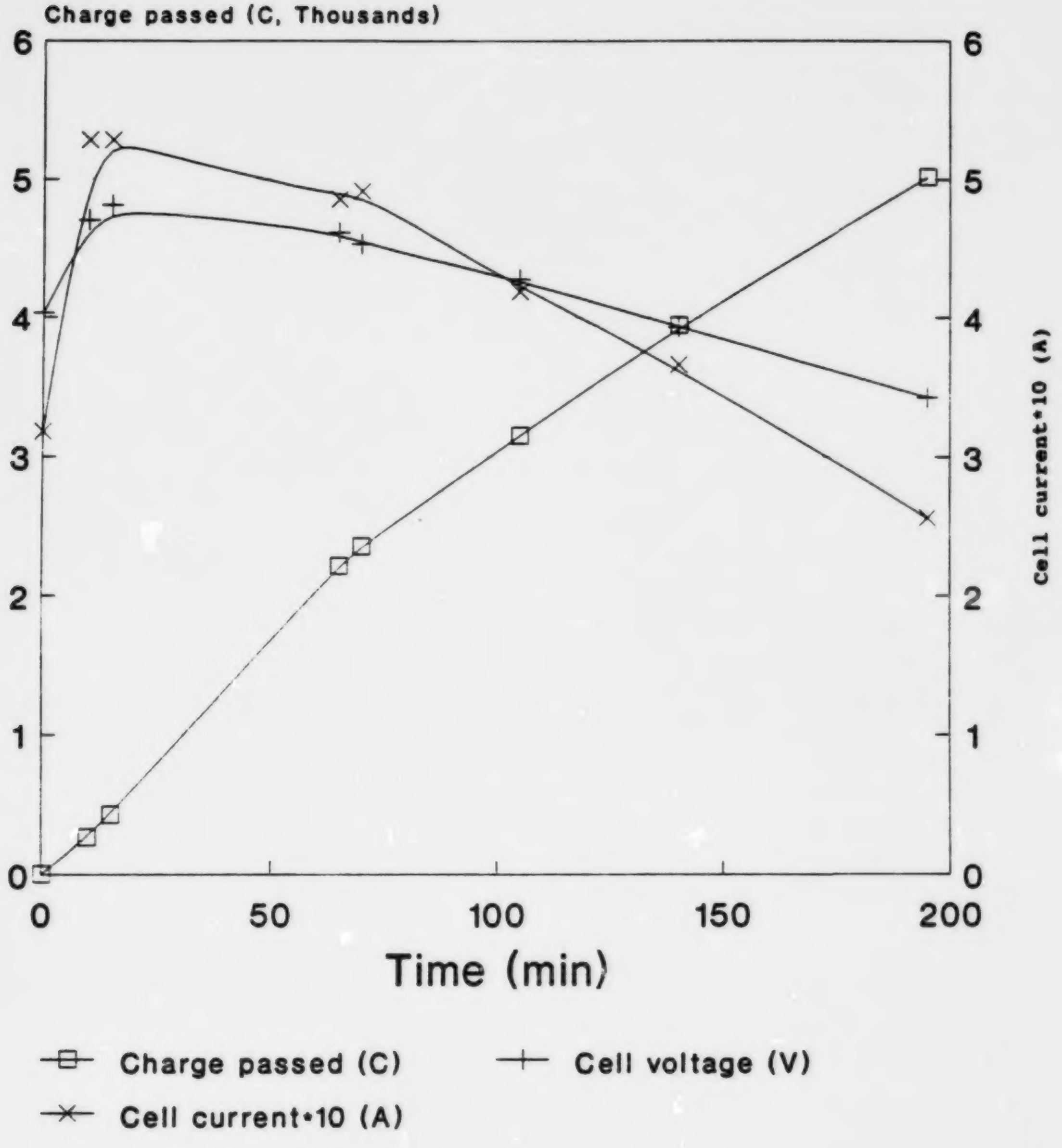


Figure 31 Total Charge Passed, Observed Current and Cell Voltage versus Duration of Electrolysis for Run S10

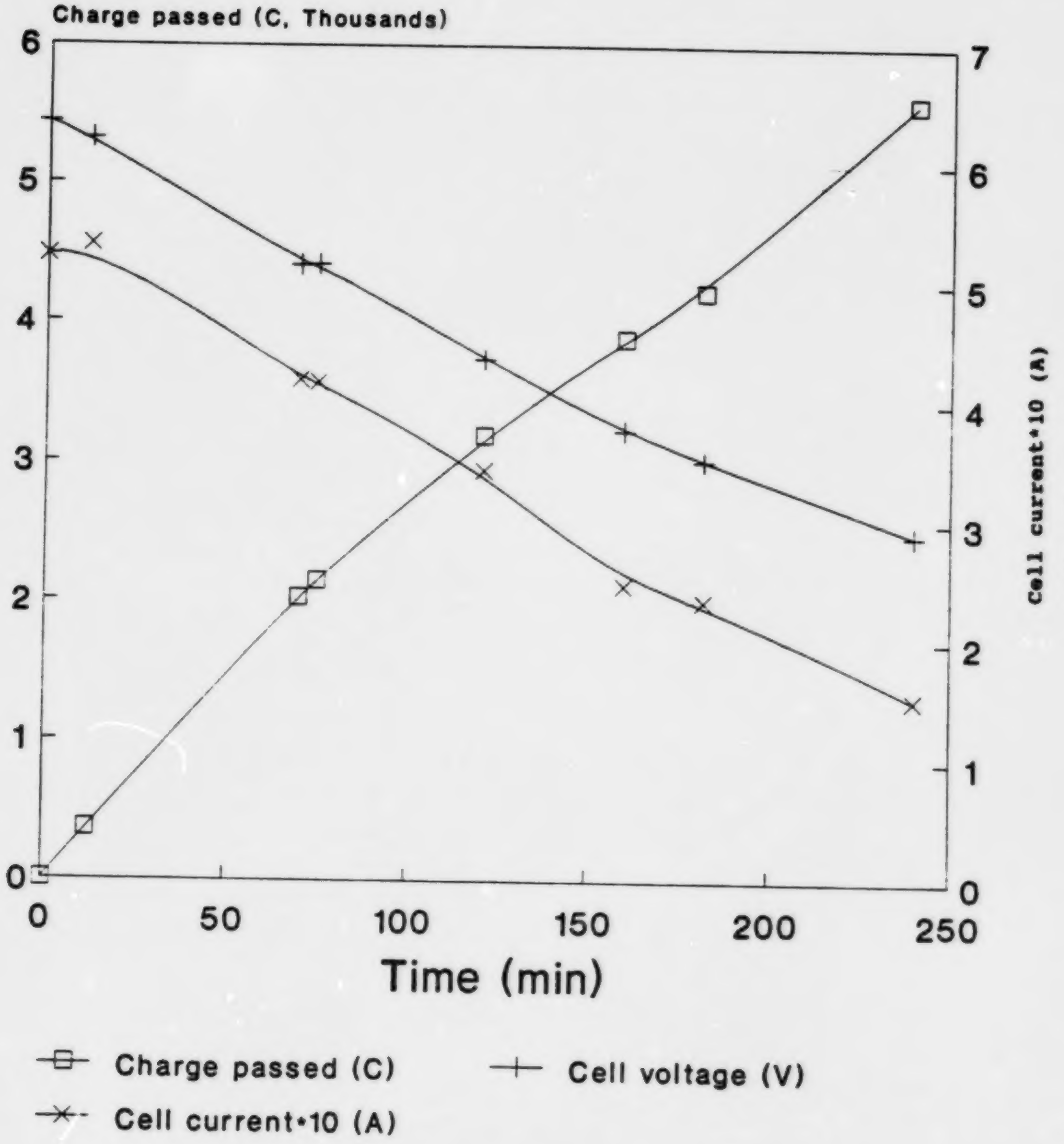


Figure 32 Total Charge Passed, Observed Current and Cell Voltage versus Duration of Electrolysis for Run S11

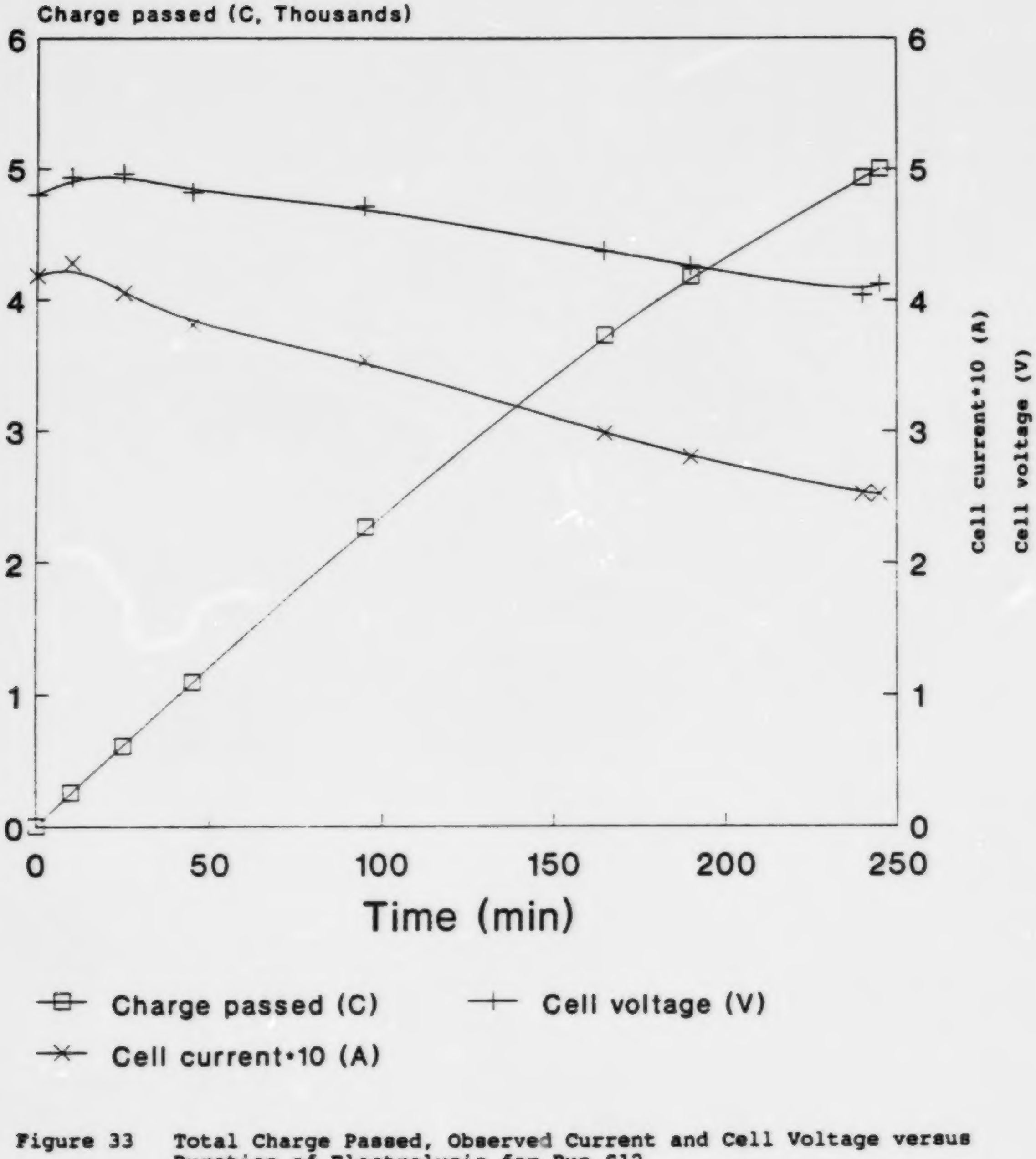


Figure 33 Total Charge Passed, Observed Current and Cell Voltage versus Duration of Electrolysis for Run S12

generated any low molecular weight chemicals of interest, see below.

3.2.3 GC-MS Analysis of Ethyl Acetate Extracts

Nine major peaks were identified in the chromatograms as succinic acid, fumaric acid, vanillin, pimelic acid, p-hydroxybenzoic acid, suberic acid, vanillic acid, azelaic acid and syringic acid by comparison of their retention times and mass spectra with authentic standards. The amounts of these compounds in the ethyl acetate extracts of the supernatant solutions obtained after acidication of the alkaline reactions mixtures of electrolyzed lignin to recovery the precipitable product are presented in Table 28.

Table 29 presents the yields of ethyl acetate solubles and the percentage of the ethyl acetate solubles accounted for by the 9 major GC volatiles. With the exception of sample S10 A, all anodic compartment samples and undivided cell samples gave ethyl acetate extracts with 12 - 16 % of the GC volatiles. Of the 9 major volatiles, the two most abundant compounds are p-hydroxybenzoic acid and azelaic acid. The amounts of these two compounds as a percentage of the total mass of the 9 major volatiles are presented in Table 30. The alkanedioic acids have been suggested to be autoxidation products of unsaturated fatty acids and have been shown to be produced by treatment of wood chips with alkali (Niemelä, 1988). This may account for the fact that the amount of azelaic acid produced is much more constant than that of p-hydroxybenzoic acid.

3.2.4 Analysis of Alkaline Electrolysis Liquors

Problems were experienced with the analysis of the alkali solutions of electrolyzed lignin and breakdown products. The peak areas of internal standards were greatly reduced in some samples and were highly variable from sample to sample making quantitation impossible. To investigate this problem,

Table 28

Hydroxy Acids, Diacids and Vanillin in Ethyl Acetate Extracts of Acidified Reaction Mixtures from Electrolysis of Lignin (mg/total extract)

Run	Sample[b]	Product[a]								
		1	2	3	4	5	6	7	8	9
S6	A	0.08	0.03	0.39	-[c]	1.90	0.08	0.21	0.45	-
S6	C	-	-	-	-	-	-	-	-	-
S7	AR	0.16	0.12	0.20	-	1.60	0.12	0.16	0.42	0.29
S7	C	-	-	-	-	0.04	-	-	-	-
S8	ARC	1.00	1.14	0.87	0.41	0.88	0.94	0.66	1.80	1.40
S9	A	0.31	0.53	0.31	0.29	0.88	0.70	0.19	1.30	0.78
S9	RC	-	-	-	-	0.09	-	-	-	-
S10	A	-	-	-	-	0.54	-	-	-	-
S10	RC	-	-	-	-	0.09	-	-	-	-
S11	A	0.45	0.52	0.17	0.24	1.50	0.58	0.34	0.99	0.87
S11	RC	-	-	-	-	0.04	-	-	0.02	-
S12	cell[d]	0.36	0.28	0.71	0.26	1.60	0.65	0.19	1.10	0.63
S13	cell[d]	0.07	-	0.51	-	1.40	0.07	0.18	0.40	0.31

[a] 1 succinic acid, 2 fumaric acid, 3 vanillin, 4 pimelic acid, 5 p-hydroxybenzoic acid, 6 suberic acid, 7 vanillic acid, 8 azelaic acid, 9 syringic acid.

[b] A = anolyte, R = reference cell solution, C = catholyte, more than one letter refers to combined solution

[c] not detected

[d] contents of undivided cell

Table 29

Mass of Ethyl Acetate Extract, Yield of Ethyl Acetate Solubles, and Percent Total Hydroxyacid, Diacid and Vanillin

Run	Sample[a]	mass of EtOAc extract (mg)	yield EtOAc solubles % lignin	mass of hydroxy acids, diacids & vanillin (mg)	% hydroxy acids, diacids & vanillin % EtOAc sol.
S6	A	22.8	2.5	3.14	13.8
S6	C	4.9	0.5	0.00	0.0
S7	A	19.3	2.2	3.07	15.9
S7	C	5.2	0.5	0.04	0.04
S8	ARC	68	7.6	9.10	13.4
S9	A	42	4.7	5.29	12.6
S9	RC	5.0	0.7	0.09	1.8
S10	A	43	4.7	0.54	1.3
S10	RC	12	1.2	0.68	5.7
S11	A	47	5.1	5.66	12.0
S11	RC	2.8	0.3	0.06	2.1
S12	cell[b]	43	4.9	5.78	13.4
S13	cell[b]	24	2.7	2.95	12.3

[a] A = anolyte, R = reference cell solution, C = catholyte, more than one letter refers to combined solution

[b] contents of undivided cell

Table 30

Production of p-Hydroxybenzoic Acid and Azelaic Acid as a Percentage of the Total Mass of the 9 Volatiles Quantified by GC-MS

Run	Sample[a]	p-Hydroxybenzoic acid (% w/w)	Azelaic acid (% w/w)
S6	A	60.5	14.3
S7	A	52.1	13.7
S9	A	16.6	24.6
S11	A	26.5	17.5
S11	RC	9.7	19.8
S12	cell[b]	27.7	19.0
S13	cell[b]	47.5	13.6

[a] A = anolyte, R = reference cell solution, C = catholyte, more than one letter refers to combined solution

[b] contents of undivided cell

standard mixtures were dissolved in strong alkali (3N NaOH) and prepared according to the procedure. The results were compared with results for the same standard mixtures derivatized directly before analysis. Sample preparation of standard mixtures by ion-exchange/derivatization of hydroxy acids and diacids in alkali gave the same results as sample preparation by direct derivatization. Variability from injection to injection was high (as high as 10 to 12%), but means of four injections of a given sample can be taken to be within 4 or 5% of the means of four injections of replicate samples.

Since the sample preparation of alkali solutions of standards has no effect on the results for standard mixtures, it was thought that the presence of lignin in the samples may account for the difficulties experienced with the electrolysis liquor samples. This was investigated by adding the lignin used as starting material or electrolyzed lignin at 1 and 10 mg per sample levels to standard mixtures and analyzing by direct derivatization and by ion-exchange/derivatization of alkali solutions.

The data from these experiments is reported in Tables 31 and 32 based on xylitol internal standard. The presence of lignin in the samples results in an increased amount of aromatic hydroxy acids in both sample preparation methods. This effect is less pronounced with the diacids. These results can be accounted for by the presence of the hydroxy acids in the lignins (contributing to the increased peak areas for these compounds) as well as some possible interaction of the xylitol with the lignin resulting in decreased peak areas for the xylitol internal standard peak. Examination of the peak areas of xylitol in the analysis confirmed a decrease in peak area in the lignin-containing samples in the direct derivatization experiment. This effect was not apparent in the ion-exchange preparation experiment, nor was it apparent when benzyl alcohol was used as internal standard. There was no underivatized benzyl alcohol in the GC traces, so incomplete derivatization

Table 31

Amounts of Diacids in a Standard Mixture Determined by Direct Derivatization and Ion-Exchange Preparation with and without Lignin Starting Material (SL) and Electrolyzed Lignin (EL)

Amount Lignin Added (Type) (mg)	Maleic Acid (mg)	Succinic Acid (mg)	Pimelic Acid (mg)	Suberic Acid (mg)	Azelaic Acid (mg)
Direct Derivatization					
0	70.0±0.9	80.4±1.7	89.4±7.7	81.0±3.8	77.5±3.1
1 SL	75.1±5.5	80.7±4.2	100.9±7.1	86.3±5.1	87.9±4.6
10 SL	74.7±3.1	84.6±6.2	95.9±9.4	91.9±5.6	86.3±8.5
10 EL	83.2±5.4	85.1±4.9	95.3±6.7	92.4±5.2	88.7±9.5
Ion-exchange Preparation					
0	90.3±8.6	91.2±2.1	107 ± 11	98.9±8.7	91.4±3.6
10 SL	97.9±8.5	96.7±7.7	119.2±6.7	109.0±6.8	102.1±6.1
10 EL	104.1±4.5	102.1±7.2	127.4±4.2	115.3±3.7	110.3±2.8

Table 32

Amounts of Hydroxy Acids in a Standard Mixture Determined by Direct Derivatization and Ion-Exchange Preparation with and without Lignin Starting Material (SL) and Electrolyzed Lignin (EL)

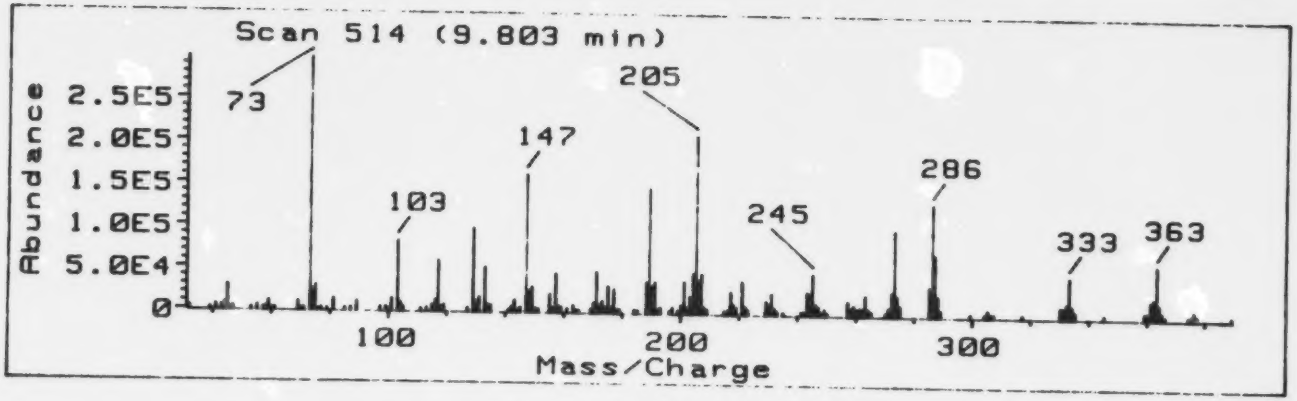
Amount Lignin Added (Type) (mg)	p-Hydroxybenzoic Acid (mg)	Vanillic Acid (mg)	Syringic Acid (mg)
Direct Derivatization			
0	129.8±3.3	93.8±7.5	95.8±2.4
1 SL	131.2±7.1	99.1±8.1	99.8±7.7
10 SL	145.7±9.6	108 ±15	104.9±7.0
10 EL	145.0±6.7	105.6±6.0	105.4±7.7
Ion-exchange Preparation			
0	133.9±6.2	108.9±8.6	109 ± 13
10 SL	143.6±6.1	111.9±6.7	125.2±5.9
10 EL	141.7±7.4	112.4±6.5	120.0±5.9

was discounted. In the case of the ion-exchange preparation, the amounts of diacids determined by this method were affected more by the presence of electrolyzed lignin in the sample than by the presence of starting lignin.

The above experiments indicate that the presence of lignin in the samples cannot account for the difficulties experienced with the electrolysis samples. Despite repeated attempts to analyze these samples and the demonstrated success of the method with standard mixtures and with the ethyl acetate solubles, quantitation was not possible for the electrolysis liquors. However, qualitatively, the following observations could be made. The four major volatiles in the ethyl acetate extracts could be detected (p-hydroxybenzoic acid, azelaic acid, syringic acid and suberic acid), often in very small amounts. Other compounds present were benzoic acid, glycerol, glyceric acid and fatty acids (especially linoleic acid and palmitic acid). By far the major peak in all GC traces of electrolysis liquor samples was an unidentified peak which eluted very shortly after xylitol and before vanillic acid. The mass spectrum (Figure 34) has many features in common with glycerol and glyceric acid at the low m/z (m/z 205 and less). This material is possibly a sugar breakdown product.

3.3 CONVERSION OF LIGNINS TO METHYL ARYL ETHERS, FUELS AND PHENOLIC COMPOUNDS (HIGHER VALUE PRODUCTS) BY OXIDATION USING PEROXYDISULFATE, ($S_2O_8^{2-}$-Cu^{II}), IN ACETIC ACID

Huynh (1986, 1988) reported the biomimetic oxidation of lignin model compounds using peroxydisulfate, ($S_2O_8^{2-}$-Cu^{II}), and suggested that this reagent was capable of depolymerizing lignin. In his study, reactions were performed in refluxing aqueous acetic acid, for 90 min, under aerobic conditions. These conditions were used "to allow oxygen to participate with free radical intermediates thus preventing the free radical coupling reactions expected to



m/z	abund.	m/z	abund.	m/z	abund.
73.1	100	189.05	49	286.1	44
103.1	26	204.15	16	287.1	24
117.0	33	205.15	70	333.15	16
147.05	54	245.1	16	363.25	20
171.05	16	273.1	33		

Figure 34 Mass Spectrum of Unidentified Product in Electrolysis Liquor Samples

occur under anaerobic conditions".

The free radical mechanisms for the oxidation of aromatics by $S_2O_8^{2-}$-Cu^{II} have been well studied, see for example, Walling *et al.* (1984) and references therein. Typically, reactions have been run under anaerobic conditions, in acetic acid (or acetonitrile)/water, at 70 to 100°C.

Acetic acid/water has long been used as a solvent for purification of lignin preparations. The use of this solvent system allows the possibility of studying the effects of the peroxydisulfate system on isolated lignin in a homogeneous reaction system. Initially, therefore, the oxidation of steam exploded aspen lignin was examined under both aerobic and anaerobic conditions. The results of these experiments are summarized in Table 33. After the reaction, the solutions of the control experiments were dark black in coloration with no obvious precipitate present. On dilution to precipitate the lignin, the solutions appeared bluish-green. Reaction mixtures with persulfate present, at 100°C, were all observed to effervesce, and a brown solid precipitated. In the reaction mixtures at 53°C, tarry brown precipitation occurred. After dilution of the reaction mixture and recovery of the precipitated materials, the chloroform extracts of the supernatent liquids from the controls gave the highest yields of extractable material, followed by the reactions at 100°C for 120 min. Extracts were examined, after silylation, by GC-MS. In the chloroform-solubles from the reaction mixtures, many components were present at very low concentrations, and in comparison with the controls several new peaks were present in the chromatograms. At the concentrations present, these compounds could not be identified.

The almost immediate precipitation of lignin from the reaction mixture on initiating the reaction at 100°C and low yields of chloroform-solubles suggests, that under the reaction conditions used, depolymerization of the steam-treated lignin was not occuring. Oxidation of 3,4-dimethoxybenzyl

Table 33

Product Yields From $S_2O_8^{2-}$-Cu^{II} Oxidation of Steam-Treated Aspenwood Lignin

	Reaction Conditions			Yield[a]	
Run	Atmos.	Temp. (°C)	Time (min)	Lignin Ppt. (wt %)	Yield $CHCl_3$ solubles (wt %)
1	air	53	30	97.2	1.33
2	air	100	30	100.3	1.23
3	air	53	120	104.0	1.51
4	air	100	120	98.8	3.09
5	nitrogen	53	30	98.4	1.64
6	nitrogen	100	30	105.2	0.53
7	nitrogen	53	120	105.1	1.00
8	nitrogen	100	120	86.1	3.24
CN_2[b]	nitrogen	53	30	97.1	6.24
CAir[b]	air	100	120	108.4	8.67

---

[a] wt % of starting material

[b] Control experiment, no persulfate salt added

alcohol (veratryl alcohol) as a model system was therefore carried out for 30 min, at 90-95°C, under nitrogen, sealed under air, and open to the atmosphere. In this reactions it was possible to observe a series of color changes to the solutions, from blue to green to yellow-brown to red-brown to brown-black. These changes occurred fastest in the nitrogen atmosphere and slowest in the tube open to the atmosphere. The chloroform soluble products were examined by GC-MS after silylation. In all three extracts the major products were veratrylaldehyde and veratryl acetate as reported by Huynh (1988). In each case there were also other products present that could not be identified readily as other products suggested by Huynh, and also higher molecular weight products formed, which contained two aromatic rings. Product analysis was not made in detail, because these experiments indicated the oxidation system was working under the conditions used and the main concern was whether it was usable with the steam-treated lignins.

To examine further what was occurring on oxidation of the steam-treated lignin with $S_2O_8^{2-}$-Cu^{II} samples of methylated (MeSEL) and acetylated (AcSEL) steam-treated lignin were prepared and oxidized with underivatized lignin (SEL) under the conditions in Table 34. Yields for the precipitated material from SEL difficult to obtain accurately, because contamination with the copper salt could be seen in some samples. This was presumably entrapped when the material precipitated during the reaction. The AcSEL and MeSEL gave lower precipitable yields than the appropriate control reaction but only the MeSEL gave increased yields of chloroform-solubles.

Weight and number average molecular weights (polystyrene equivalents) and polydispersities are presented in Table 35. The data can be grouped into four categories (Figure 35). The precipitated reaction products from SEL gave similar data to each other, but it was meaningless, because only a small portion of these samples was soluble in THF after acetylation (category 1). The starting and control samples of SEL had a weight average molecular weight

Table 34

Product Yields From $S_2O_8^{2-}$-Cu^{II} Oxidation of Steam-Treated Aspenwood Lignin, Methylated Steam-Treated Aspenwood Lignin, and Acetylated Steam-Treated Aspenwood Lignin

Lignin Type	Reaction Cond. Atmos	Reaction Cond. Time (h)	Yield[a] Lignin Ppt.	Yield[a] $CHCl_3$-solubles	Yield[a] Total
SEL[b]	air	2	78.2	13.1	91.3
SEL	air	2	102.8	1.5	104.3
SEL	air	4	92.2	1.9	94.2
SEL	N_2	2	106.1	1.9	108.0
AcSEL[b]	air	2	89.0	9.4	98.4
AcSEL	air	2	80.0	7.4	87.5
AcSEL	air	4	69.5	7.7	77.3
AcSEL	N_2	2	78.4	6.3	84.7
MeSEL[b]	air	2	89.4	8.6	97.9
MeSEL	air	2	80.8	11.5	92.3
MeSEL	air	4	77.4	10.6	88.0
MeSEL	N_2	2	86.5	10.8	97.3

[a] wt % of starting material

[b] Control reaction, no ammonium persulfate added

Table 35

Weight and Number Average Molecular Weights (Polystyrene Equivalents) and Polydispersities of Precipitated Products from $S_2O_8^{2-}$-Cu^{II} Oxidation of Steam-Treated Aspenwood Lignin, Methylated Steam-Treated Aspenwood Lignin, and Acetylated Steam-Treated Aspenwood Lignin

Lignin Type	Reaction Cond. Atmos	Time(h)	Molecular Weight distribution M_w	M_n	M_w/M_n
SEL[a]			5814	589	9.9
			6025	597	10.1
SEL[b]	air	2	5423	574	9.5
			5427	562	9.7
SEL[c]	air	2	367	233	1.6
			367	231	1.6
SEL	air	4	300	195	1.5
			316	197	1.6
SEL	N_2	2	286	185	1.6
			285	189	1.5
AcSEL[d]			7994	1314	6.1
			9840	1466	6.5
AcSEL[b,e]	air	2	6998	1202	5.8
			9081	1488	6.1
AcSEL	air	2	2300	455	5.1
			2493	470	5.3
AcSEL	air	4	2291	513	4.5
			2526	543	4.7
AcSEL	N_2	2	2486	535	4.7
			2902	553	5.2
MeSEL[f]			7619	1150	6.6
			9835	1351	7.3
MeSEL[b]	air	2	6549	1070	6.1
			7645	1198	6.4
MeSEL	air	2	2148	588	3.7
			2350	611	3.9
MeSEL	air	4	2326	644	3.6
			2703	685	4.0
MeSEL	N_2	2	2368	627	3.8
			2801	695	4.0

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[a] Starting material, acetylated by method with evaporation of reagents, i.e. no precipitation step.

[b] Control reaction, no ammonium persulfate added

[c] Precipitated product, acetylated for HPSEC by method with evaporation of reagents. After acetylation all precipitated products from oxidations of SEL had poor solubility in THF.

[d] Starting material made by acetylation method with dilution to precipitate lignin.

[e] Precipitated products from oxidations of AcSEL and MeSEL did not require further derivatization to determine molecular weight data, being completely soluble in THF.

[f] Starting material.

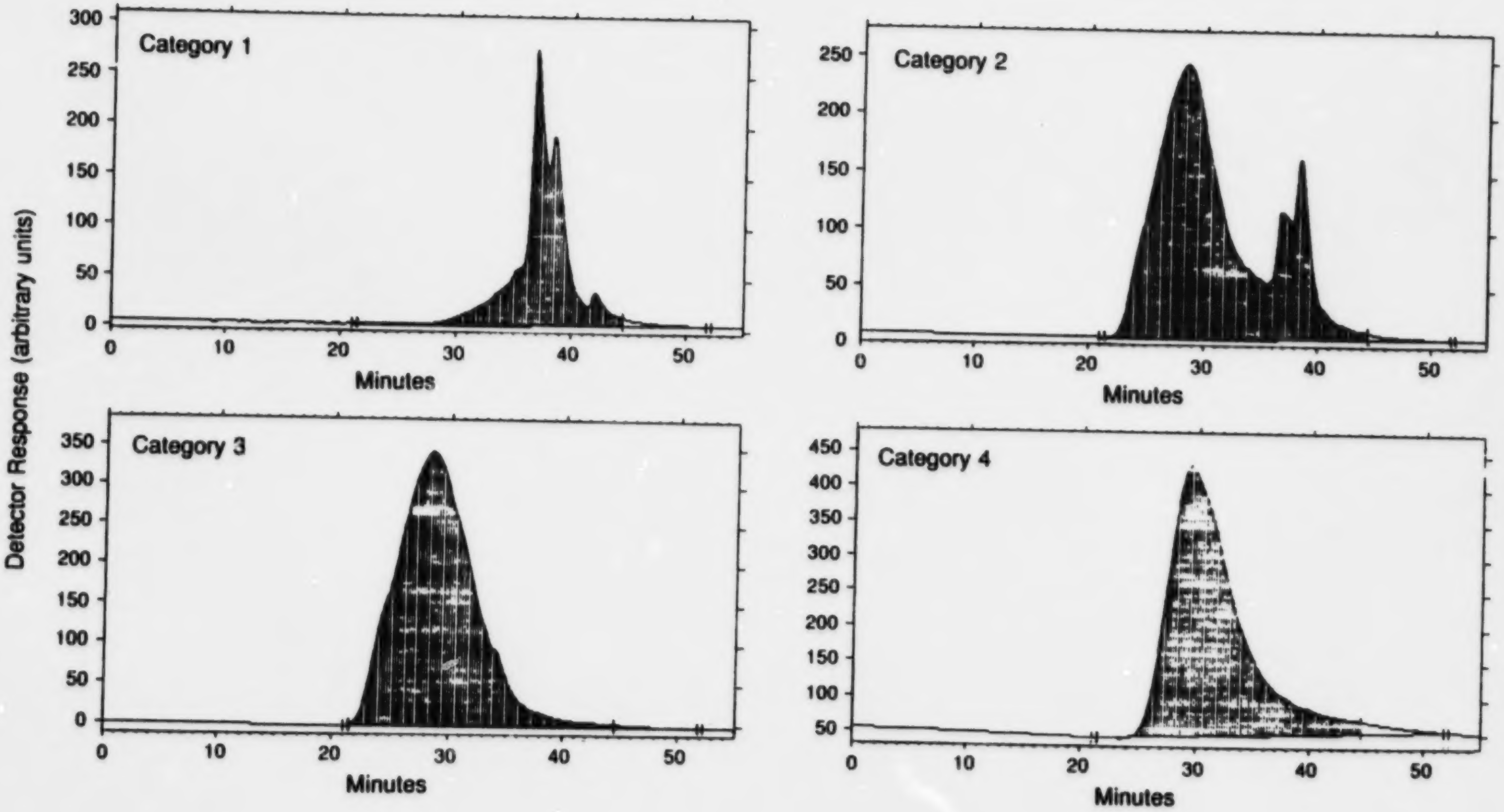

Figure 35 Categories of HPSEC Profiles Obtained for Products from $S_2O_8^{2-}$–Cu^{II} Oxidation of Steam-Treated Aspenwood Lignin, Methylated Steam-Treated Aspenwood Lignin, and Acetylated Steam-Treated Aspenwood Lignin

of 5670 ± 300 and a polydispersity of 9.8 ± 0.3. However, the distributions were bimodal because of the presence of low molecular weight material (category 2). This low molecular weight material was absent from the derivatized starting materials and control samples, which were derivatized and purified by precipitation, leaving the low molecular weight material in solution. These samples make up the third category. The average weight average molecular weight of these controls were 8150 ± 1200 and their polydispersities were 6.4 ± 0.5. These data are directly comparable to the fourth catagory which consists of the persulfate oxidized acetylated and methylated lignin samples. The weight average molecular weights of these samples were 2480 ± 230 and their polydispersities were 4.4 ± 0.6. This indicates that persulfate oxidation of methylated and acetylated lignins results in over a threefold decrease in the weight average molecular weights of the acetylated and methylated lignin samples and over a twofold decrease in their number average molecular weights. Acetylated and methylated lignins were depolymerized to the same extent.

These results and the observations in the reactions of the precipitation of the underivatized SEL from the reaction mixture to a product that could not be acetylated to a soluble derivative for HPSEC, demonstrated that the product of oxidation is dependent on the available functional groups within the lignin, and can either lead to substantial depolymerization when the available hydroxyl functions are blocked (presumably phenolic hydroxyls) and polymerization when they are available.

Infrared spectra were recorded for the precipitated lignin products. There were no differences in the spectra for each set of precipitated lignins from SEL, AcSEL and MeSEL. The only major difference between the products and the respective starting materials were in the increased intensity of absorption bands in the carbonyl region (1600-1800cm^{-1}) (examples are shown in Figure 36). Unfortunately, resulting from equipment problems, these spectra were

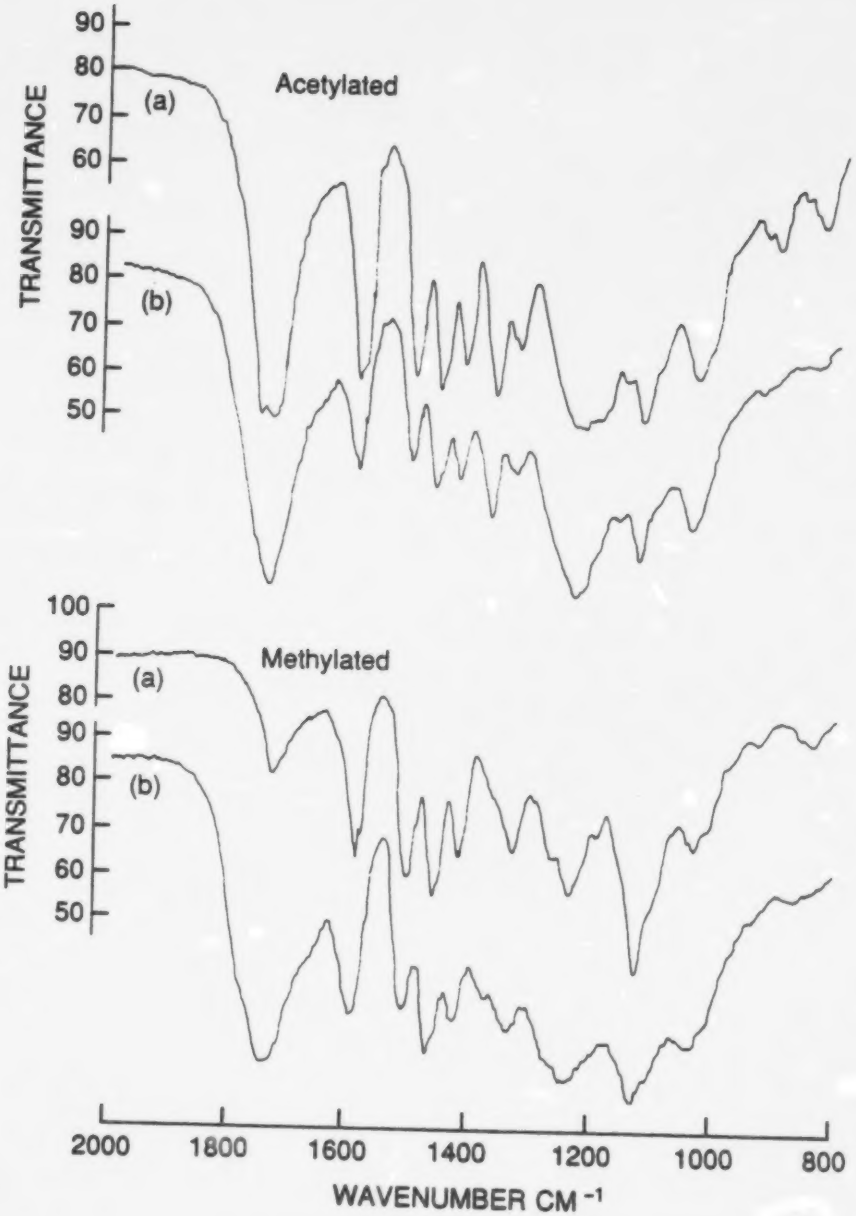

Figure 36 IR spectra of Starting Materials (A) and Precipitated Products (B) from $S_2O_8^{2-}$-Cu^{II} Oxidation of Acetylated Steam-Treated Aspenwood Lignin, and Methylated Steam-Treated Aspenwood Lignin

recorded on an old grating spectrometer and were of low quality, thus differences in peak intensities and slight shifts in band positions were not investigated further.

Different low molecular weight compounds were produced from the different starting materials. The distribution of these compounds as a percentage of the internal standard is given in Table 36. Few products could be identified from the mass spectral data. In the products from MeSEL, relatively high yields of 3,4,5-trimethoxybenzoic acid were present, and lower quantities of 3,4-dimethoxybenzaldehyde, 3,4,5-trimethoxybenzaldehyde, and 4-hydroxy-3-methoxy-benzoic acid. The analysis was not taken further because of the low yields of chloroform-solubles obtained from these reactions.

3.4 OXIDATION OF LIGNIN MODEL COMPOUNDS WITH METALLOPORPHYRINS

Biochemical mechanisms of lignin degradation have been extensively studied for white rot fungi, in particular *Phanerochaete chrysosporium*. Two types of extracellular heme-containing enzymes play important roles in the decay of lignin by white rot fungi. These enzymes are peroxidases and include a group of ligninases (or "lignin peroxidases") and a group of manganese peroxidases.

From studies with model compound, ligninases appear to initiate lignin degradation by extracting one electron at a time from methoxylated aromatic rings, forming radical cation species, which undergo further non-enzymatic reactions that lead to lignin decomposition.

Synthetic tetraphenylporphyrin iron (III) chloride in combination with iodosylbenzene or *tert*-butyl hydroperoxide (TBH) in an organic solvent was demonstrated to cleave, in the same manner as ligninase does, the $C\alpha$-$C\beta$ bonds in the side chains of diarylpropane lignin model compounds (Shimada *et al.*,

Table 36

Distribution of Low Molecular Weight Products in the Chloroform-Solubles from the $S_2O_8^{2-}$-Cu^{II} Oxidation of Steam-Treated Aspenwood Lignin, Methylated Steam-Treated Aspenwood Lignin, and Acetylated Steam-Treated Aspenwood Lignin as a Percentage of Internal Standard

	CHLOROFORM-SOLUBLES FROM REACTION AS PERCENTAGE OF INTERNAL STANDARD											
	SEL				AcSEL				MeSEL			
GC Ret'n Time (min)	Control Air	2 Air	4 Air	2 N_2	Control Air	2 Air	4 Air	2 N_2	Control Air	2 Air	4 Air	2 N_2
7.63[a]										4.43	1.78	
7.99										1.47	1.99	1.65
8.33											7.23	6.02
8.42										3.81	3.35	3.56
8.72[b]									2.80	6.07	2.61	2.02
8.85	2.8					7.08	4.58	3.74				
9.19										1.64	2.07	2.55
9.30										2.71	2.08	2.10
9.45											8.81	8.35
9.60	INTERNAL STANDARD											
9.75		2.20		2.59						3.19		2.11
9.99[c]						3.24	6.92				2.36	
10.09						8.31	6.85	6.53				
10.15[d]		9.74	6.79	10.92		7.31	7.64	4.33		2.94	3.30	3.28
10.43[e]									6.19	25.22	29.06	27.69
10.72	4.32								4.32			
10.99	2.80	1.71	1.63	2.14		3.95	5.31	2.02	2.80			1.96
11.27					3.32							
11.28							1.88					
11.71											1.23	
11.85	2.68								2.68			
13.07	3.98				2.88							
13.17	1.99											
13.23	3.91											
13.65	2.05											
13.69	3.89											
14.39								4.9				
15.33											2.56	2.74

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[a] 3,4-dimethoxybenzaldehyde
[b] 3,4,5-trimethoxybenzaldehyde
[c] 4-hydroxy-3-methoxybenzoic acid (silylated derivative)
[d] Azelaic acid, TMS derivative
[e] 3,4,5-trimethoxybenzoic acid

1984). Hemin in the presence of hydrogen peroxide or TBH was subsequently found to mimic ligninase in the same bond cleavage (Habe *et al.*, 1985b). Treatment with heme and TBH in aqueous solutions at reflux of softwood Kraft pulps or birch wood chips resulted in delignification (Paszczynski *et al.*, 1988). In these studies a selection of metal based heme compounds was used including: iron, manganese, copper, nickel, cobalt, and zinc. In earlier work, related to cytochrome P450-dependent reactions, iron-porphyrin catalysis of the deaklylation of substituted anisoles and ethoxycoumarins by cumyl hydroperoxide or TBH to the corresponding phenol were reported (Mansuy *et al.*, 1980).

Initially, a number of experiments were attempted using simple methoxylated benzenes and a range of metal porphyrin derivatives under conditions similar to those of Shimada *et al.* (1984) to determine whether any demethylation, demethoxylation or other reactions occurred.

3.4.1 Oxidations using TPPFeCl

Methoxybenzene (Anisole) gave no oxidized product, but in the gas chromatogram of the reaction products low levels of benzoyl chloride (impurity from TPPFeCl?) and a chloromethoxybenzene were present (Figure 37). In published mass spectra (Korhonen *et al.*, 1988), for ortho and para substituted anisoles the molecular ion peak constitutes the base peak and the dominant primary fragmentation reaction is the loss of CH_3 radical whereas anisole and meta substituted anisole preferentally eliminate CH_2O. From consideration of the relative ratios of the ions present from the subsequent fragmentation (loss of CO) to yield ion m/z = 99, the product is tentatively identified as 2-chloroanisole.

In the control reactions (no added TBH, and no added TPPFeCl) only the starting material was detected in the chromatogram of the products.

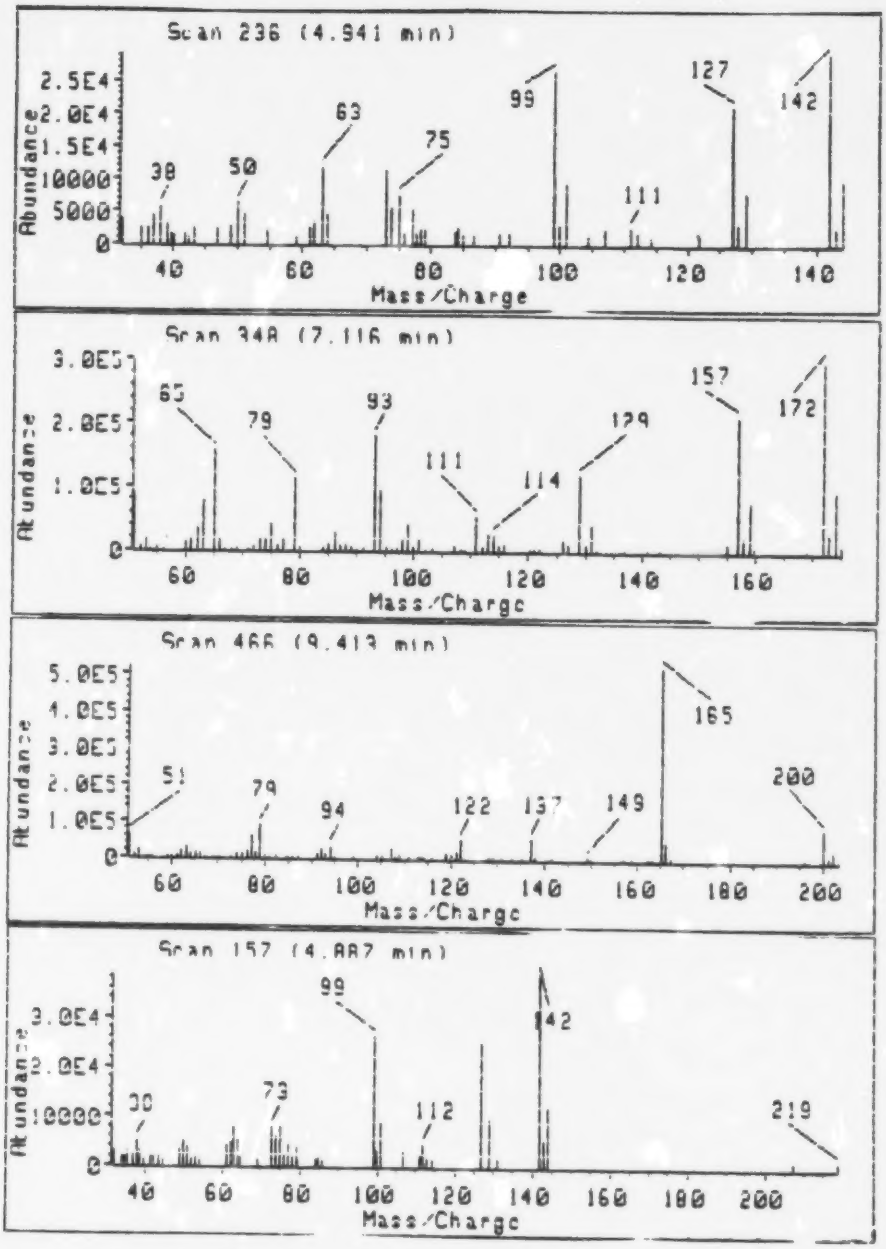

Figure 37 Mass Spectra of Chlorinated Products Detected on Oxidation of Lignin with Metalloporphyrins: (A) Chloromethoxybenzene from reaction of TPPFeCl with methoxybenzene; (B) 4-chloroveratrole from reaction of TPPFeCl with 1,2-dimethoxybenzene; (C) 3,4-dimethoxybenzoyl chloride from reaction of TPPFeCl with 3,4-dimethoxybenzaldehyde; and (D) 2-chloroanisole from reaction of TPPMnCl with methoxybenzene

1,2-Dimethoxybenzene (Veratrole) yielded only starting material and a chlorinated product (Figure 37). The chlorinated product has an intense molecular ion (142) typical of a chloroveratrole (Knuutinen and Korhonen, 1987). From the ratio of the ions corresponding to $[\text{M-CH3-CO-CH3}]^+$ and $[\text{M-CH3-CO-H2O}]^+$, $([\text{M-58}]^+/[\text{M-61}]^+$, the product is tentatively identify as 4-chloroveratrole.

In the control reactions (no added TBH, no added TPPFeCl) only starting material was recovered.

In the gas chromatogram of the reaction mixture from 3,4-dimethoxybenzaldehyde (veratraldehyde) the dominant peak was the starting aldehyde. Two products were also present. One was the expected oxidation product 3,4-dimethoxybenzoic acid, the second was a chlorinated compound (Figure 37). The mass spectrum of this material has a molecular ion at m/z 200, and the characteristic intensity with m/z 202 for the presence of one chlorine atom. Because the primary fragmentation of the parent ion (165) is loss of chlorine, and the second major fragmentation is to $[\text{M-Cl-CO}]^+$, (m/z 137), the compound is tentatively identified as 3,4-dimethoxybenzoyl chloride.

In the control reactions only the starting aldehyde was detected.

Reactions with 3,4-dimethoxybenzyl alcohol (veratryl alcohol) gave a mixture of products which could not be interpreted. The starting alcohol was also contaminated with the corresponding aldehyde.

3.4.2 Oxidations using Hemin

These reactions gave only very low intensity product peaks in the gas chromatograms. For anisole, in addition to starting material only trace amounts of either the 2- or 4-chloroanisole were detected. With 1,2-

dimethoxybenzene only this plus an unidentifiable product were detected. For the reaction containing 3,4-dimethoxybenzaldehyde the starting material was recovered with some of the corresponding acid and trace quantities of the corresponding monochloroinated derivatives. With 3,4-dimethoxybenzyl alcohol results were again complex and a small quantity of the corresponding acid may have been formed.

3.4.3 Oxidations with TPPMnCl

For the reaction containing anisole, the only materials present in the chromatogram of reaction mixture were the starting material and 1-chloro-2-methoxybenzene (2-chloroanisole) (Figure 37), which was identified by computer search of NBS library spectra. Control reactions only contained starting material. With 1,2-dimethoxybenzene the only identifiable product besides starting material is tentatively identified as 4-chloroveratrole. The control reactions only contained starting material. For 3,4-dimethoxybenzaldehyde the major peak present in the chromatogram was the oxidation product 3,4-dimethoxybenzoic acid. A component present at trace levels is tentatively identified as 3,4-dimethoxybenzoyl chloride (Figure 37). Several other unidentified components at trace levels were observed.

For 3,4-dimethoxybenzyl alcohol, in the reaction mixture high conversion to dimethoxybenzaldehyde and traces of 3,4-dimethoxybenzoic acid were observed. However, in the control with TBH present similar conversion was observed. Only starting material was observed in the control only with the metal complex present, suggesting this system may be undergoing oxidation without catalyst present. This was also observed in one other system (see below).

3.4.4 Oxidations with TPPCu and TPPVO

With these two complexes no reactions were observed except for TPPVO with 3,4-dimethoxybenzaldehyde. For this system apart from the starting aldehyde only a small yield of the corresponding acid was indicated, but in the control with TBH present the identical gas chromatogram was obtained. In the metal salt control only starting material was observed. Again this indicates that in the system the product observed is coming from an oxidation in which the metal salt is not involved.

These experiments raise several points of concern: firstly, the observation of trace quantities of chlorinated products; secondly, the observation in two cases of oxidation in the absence of metal complex; thirdly, the observation that when oxidation occurred only very low conversions were obtained and products were dependent on the starting material. The first and second observations may both result from reactions occurring in the injection port of the GC used for the analysis of the reaction mixtures. Because of these observations these oxidation systems were not used on lignin.

A disadvantage of using heme based systems such as protohemin or tetraphenylporphyrin iron chloride is that they are easily destroyed by oxidants and therefore have short life times. Recently, water-soluble hemins, for example, meso-tetra(2,6-dichloro-3-sulfonatophenyl)porphyrin iron chloride, have been shown to catalyze many oxidation cycles of model lignin compounds without significant destruction (Cui and Dolphin, 1991). This heme compound is also soluble in both aqueous and polar organic solvents. The oxidation of model lignin compounds using this catalyst were found to be dependent on pH and the solvent being used. This type of synthetic heme catalyst merits further attention and should be evaluated on available types of lignin in both aqueous and organic systems.

3.5 PRELIMINARY EVALUATION OF FRACTIONATED LIGNIN ADHESIVES FOR WOOD COMPOSITE PANELS

A few years ago it was demonstrated that waferboard panels of excellent quality could be obtained using lignin-based adhesives (Dolenko and Clarke, 1978; Shen and Calvé, 1980). However, PF resin producers have continued working at improving their resin formulations. In the early 1980's press cycle times of 6-7 min for 11.1 mm panels were being used, but now these have now been reduced to 3-4 min. To be acceptable to industry new fast curing lignin-based adhesives must be developed. Recently at Forintek, it was found that faster curing lignin-phenolic resins could be formulated if a mixture of high and low molecular weight phenolic resins was employed as a crosslinker. With this type of crosslinker, 10-15 % PF replacement with lignin, without impairing the panel properties was possible. It was further discovered that larger quantities of lignin (20-30 %) could be used for the formulating of face resins for three layer waferboards. To be used as a face resin, an adhesive must be pre-cure resistant so that it will not cure at first contact with the hot press platens before sufficient pressure is present to consolidate the mat. Although lignins derived from pulp and paper processes have shown some potential for the development of commercial lignin-based adhesives, other sources of lignin which may be more reactive and possibly obtained under more controlled conditions, might be more suited in this application. If the lignins were more reactive, higher percentages of PF could be replaced. A lignin produced under more controlled conditions will avoid variations in resin adhesive properties, an essential condition for its acceptance by the panel products industry.

This section summarizes the preliminary test results for particleboards bonded with adhesives incorporating lignin-fractions obtained by ultrafiltration. This study must be considered only as a screening step since panels of very small dimensions (35 x 69 x 11.1 mm) were produced and only wet torsion shear tests and percent thickness swelling measurements after two hour boil are reported. The technique used was developed for the evaluation of the adhesive properties of small quantities (0.5 - 2 g) of material (Calvé 1989).

Wet torsion shear is a good indicator of the curing characteristics of a resin because it relates to the mechanical strength properties at the center layer of a panel, which is where undercuring generally occurs. Thickness swelling after two hours boiling is also an indication of the degree of crosslinking and insolubilization of a resin. A fast curing resin should crosslink and insolublize during the pressing of the panel and should yield test samples with low thickness swelling and high torsion shear strength. It should be emphasized that the results of this study are the average of only four torsion shear tests or thickness swelling samples from only two miniature particleboard panels obtained from a single wood particle-resin blend.

3.5.1 Effect of Molecular Weight Range of Lignin

Table 37 summarizes the test results for particleboards bonded with the adhesives incorporating the multiple batch and constant volume ultrafiltered lignin-fractions, the unfractionated lignin, and the softwood kraft lignin control and control PF. The highest molecular weight lignin-fractions from the ultrafiltrations (>100) could not be assessed by the methods used because of their insolubility in the solvents used in preparing the resins. In agreement with previous findings (Calvé and Brunette, 1986; Sellers 1989; Sutcliffe and Calvé, 1990) the low molecular weight lignin-fractions (<30K) from both the multiple batch and constant volume ultrafiltrations appear more reactive than the higher molecular weight fractions (30-100K) as indicated by slightly higher torsion shear test results and lower thickness swelling obtained at both 3 and 5 min press cycles for the particle board specimens bonded with the lower molecular weight fraction lignin based resins. Relatively high torsion shear and low thickness swelling were obtained for the

Table 37

Effect of Lignin Molecular Weight on Adhesive Properties of Lignin (40 %) - PF (60 %) Resin

Lignin		Board Properties			
Type	Mol. wt. range	Press cycle (min)	Density (kg/m^3)	Thickness swelling (%)	Wet torsion shear (N.m)
Aspenwood lignin					
Unfractionated	-	3	738	21	3.3
		5	742	16	6.1
Batchwise UF	<30K	3	761	22	3.5
		5	776	16	5.8
	30-100K	3	749	29	3.1
		5	741	19	4.7
	>100K	3	n.d.[a]	n.d.	n.d.
		5	n.d.	n.d.	n.d.
Constant volume UF	<30K	3	753	23	4.0
		5	751	14	6.1
	30-100K	3	742	22	3.1
		5	745	17	5.3
	>100K	3	n.d.	n.d.	n.d.
		5	n.d.	n.d.	n.d.
Softwood kraft					
Unfractionated	-	3	769	33	2.8
		5	767	19	4.7
Control					
PF crosslinker	-	3	741	14	6.8
		5	737	8	5.5

[a] not determined because of insolubility of lignin-fraction

unfractionated lignin adhesive samples in comparison to the fractionated lignin materials. Based on the results of this study, unless the low molecular weight fraction is available at low cost, there may be no significant advantage in fractionating the lignin by UF to formulate lignin-PF adhesives. Of course this should be verified by manufacturing and testing larger scale panels. A small difference obtained with the miniature particleboards may result in a significant difference for the larger panel. The test results obtained with the unfractionated kraft lignin were disappointing as relatively high thickness swelling and low torsion shear strength were observed.

3.5.2 Effect of Lignin-PF Ratio

Figures 38 and 39 show the effect of lignin-PF ratio on percent thickness swelling and wet torsion shear strength. As expected, increasing the lignin content in the resins resulted in increasing the thickness swelling and produced lower torsion shear test results. These results, however, indicate that under these experimental conditions 10 to 20 % unfractionated lignin could be substituted into the PF resin without affecting its curing properties.

3.5.3 Comparison Between Commercial and Experimental Resins

Table 38 summarizes the test results for particleboard bonded 3 min at 210°C with a commercial face PF resin (used as face adhesive for the manufacture of three layer waferboards) and with the lignin (30 %)-PF (70 %) resin prepared in this study. Both resins tested under the same conditions yielded panels with similar thickness swellings and wet torsion shear strengths. These results suggest that unfractionated aspenwood lignin could be used to formulate a face resin with 30 % PF substitution for waferboard application.

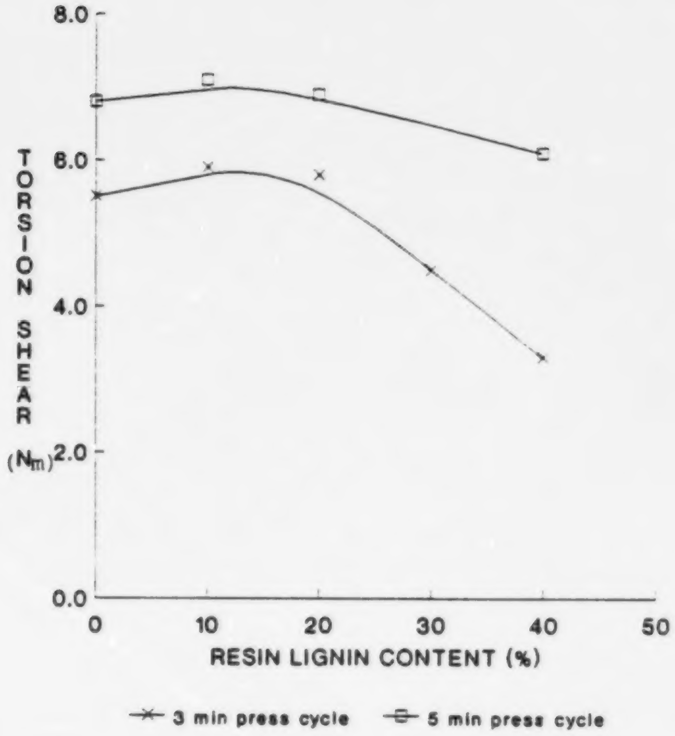

Figure 38 Effect of Resin Lignin Content on Torsion Shear

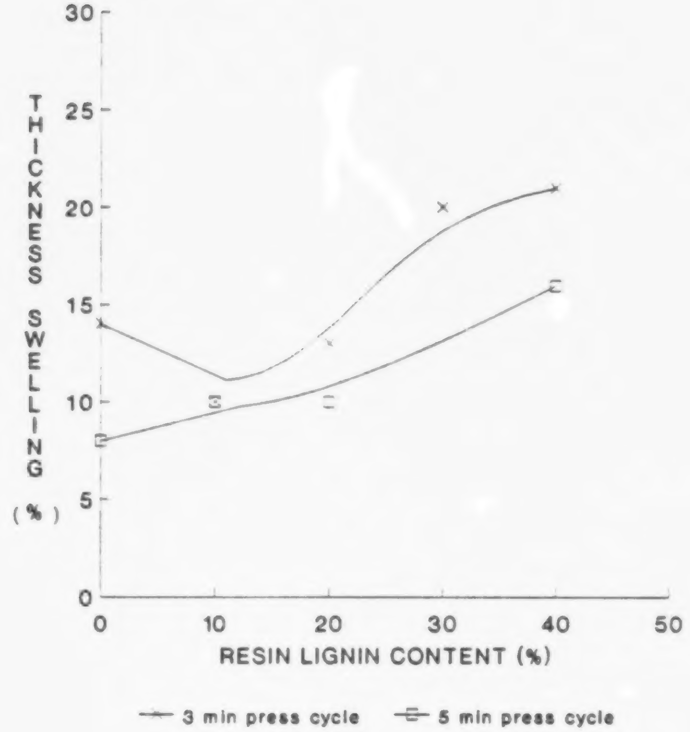

Figure 39 Effect of Resin Lignin Content on Thickness Swelling for Samples Boiled for Two Hours

Table 38

Properties of Particleboards Bonded with Unfractionated Aspenwood Lignin (30 %) - PF (70 %) and Commercial Face Waferboard Resin*

RESIN	Board Properties			
	Press cycle (min)	Density (kg/m^3)	Thickness swelling (%)	Wet torsion shear (N.m)
Lignin (30 %) - PF (70 %)	3	743	18	4.5
Commercial face PF	3	738	24	4.2

* BD 802 from Reichhold Ltd.

3.6 EVALUATION OF STEAM-TREATED LIGNIN AS A "PRE-CURE" RESISTANT SURFACE ADHESIVE FOR THREE-LAYER WAFERBOARD

At Forintek, research and development work has shown that it is possible to take advantage of the lignin chemical structure in the formulation of high quality lignin-phenolic adhesives. Methods to control the speed of cure and pre-cure resistance of lignin-phenol-formaldehyde resins have been developed (Calvé, 1991a, 1991b). It is important that the resin utilized for bonding the face layers of a three-layer waferboard be pre-cure resistant. If a resin cures prematurely while the mat is resting on a hot caul plate and before pressure is applied to consolidate the mat, a poor bond will ensue. Also, to be acceptable at the industrial scale, a surface adhesive, in addition to being pre-cure resistant, must possess a suitable curing speed and develop a bond strength comparable to existing phenolic adhesives. In a previous study, it was shown that steam-treated aspenwood lignins cross-linked with a binary phenolic resin had curing and strength properties similar to a surface adhesive for three-layer waferboards (Sutcliffe and Calvé, 1990). In this study, the possibility of producing a pre-cure resistant waferboard surface adhesive from steam-treated lignin, an ammonium salt, and a phenol-formaldehyde resin was investigated. The potential of various steam-treated aspenwood lignins was examined and one formulation selected. The resulting lignin-phenol-formaldehyde-ammonium salt adhesive was compared for pre-cure resistance speed of curing and quality of the bond to a commercial face phenolic adhesive presently employed for the manufacture of waferboard in Canada.

Resin manufacturers produce a surface phenolic adhesive by adding expensive chemicals (over $1.00/kg) to phenol-formaldehyde in order to adjust the speed of curing and pre-cure resistance. This may be accomplished by adding lignin and a salt such as ammonium sulfate, which are less expensive (for example, ammonium sulfate costs approximately $0.40/kg). Of course, it is also possible to produce a surface lignin-phenolic adhesive with pre-cure resistance by adding expensive chemicals, such as those employed by resin manufacturers. In fact, this type of resin was successfully evaluated in a waferboard mill in a previous study (Calvé *et al.*, 1991). The nature of the chemicals employed by industry is generally kept confidential.

The fusion test as described in Appendix 4.1 provides some information about the fluidity of a fusible, thermal setting resin. Before cross-linking into an infusible mass, a waferboard adhesive should become liquid to "wet" the wood and form a continuum of wood-resin-wood. The lignin-phenol-formaldehyde resin prepared in this study had a fusion test of 21-24 mm, which was observed to be independent of lignin-molecular weight or pretreatment (Table 39). In the presence of the ammonium salt, the RS4-PF resin had a fusion test of 31mm which is comparable to the control resin.

During the stroke cure test, the resin is stroked back and forth on a metal plate maintained at 150°C. As indicated in Table 39, a face resin generally has a stroke cure of 38-40 s, compared to 15-30 s for a core resin. Again the presence of ammonium sulfate was beneficial as it increased the stroke cure from 28 s for RS4-PF to 38 s. The RS4 lignin was selected for further work because it yielded a lignin-PF resin with a relatively long stroke cure test (see Table 39) even without the higher concentration of ammonium sulfate, and because at that time the use of SO_2 in steam pretreatment research was believed to be the most favorable substrate for enzymatic hydrolysis.

The strength properties of homogeneous waferboards bonded with the lignin RS4-PF resin with 4.5% salt and the BD802 reference are summarized in Table 40. For all the panels produced, even those at a short press cycle of 3 min, the lignin extended adhesive compared advantageously with the commercial surface PF resin. The waferboards yielded similar test results for all the properties evaluated (MOR, MOE, wet MOR and IB).

Table 39

Cure Plate Test and Fusion Test Results for Lignin-PF Adhesive[a]

Adhesive type	Cure plate test[b] (s)	Fusion test[c] (mm)
RS1-PF	31	23
RS2-PF	22	21
RS3-PF	22	21
RS4-PF	28	23
RS5-PF[d]	nd	nd
RS6-PF	30	24
RS7-PF	25	22
RS8-PF[d]	nd	nd
RS4-PF + 4.5% salt	39	31
BD802	39	31

[a] Lignin (30%)-PF(70%)

[b] Number of seconds to cure at 150°C

[c] Diameter of fused lignin-PF at 150°C

[d] Lignin would not dissolve to make adhesive, therefore, not determined

Table 40

Mechanical Properties of Homogeneous Waferboards Bonded with Lignin RS4-Phenol-Formaldehyde-Ammonium Sulfate (4.5%) Resin

Adhesive type	Press time (min)	MOR (MPa)	Wet MOE (MPa)	MOR (MPa)	IB (MPa)
RS4-PF 30%-70%	3	23.4	4127	10.2	0.219
	4	26.3	4284	15.3	0.469
	5	29.4	4673	15.7	0.528
BD802	3	18.1	3774	--[a]	0.159
	4	28.3	4969	12.6	0.462
	5	29.9	4916	13.7	0.508
CAN3-0437.0-M85		17.2	3100	8.6	0.345

[a] Delamination

The lignin-PF-ammonium sulfate (4.5%) resin also possesses some pre-cure resistance (Table 41). Waferboards bonded with the experimental adhesive had less surface flaking and higher internal bond strength than the panels prepared with the commercial surface resin.

3.7 STEAM EXPLODED LIGNIN AS A NEW ADDITIVE FOR BUILDING MATERIALS (SUB-CONTRACT)

Unfractionated lignin and lignin-fractions were provided to Concordia University during this contract. The work plan and report are contained in Appendix 4.5.

4.0 CONCLUSIONS

Batch ultrafiltration of alkaline extracts of steam-treated aspenwood water-insolubles yields polydisperse fractions. A substantial low molecular weight component may be present in the highest average molecular weight fractions. The characteristics of the fractions obtained by ultrafiltration suggest that it may be inappropriate to fractionate this type of lignin into more than two or three fractions. The yields from constant volume and multiple batch ultrafiltrations of the alkaline extracts are similar, but not directly comparable with the yields from the fractionation of the ethyl acetate-extracted lignin and not comparable with the original ultrafiltration experiments. The results of constant volume and multiple batch ultrafiltrations suggests that there is a lignin or alkali concentration dependence to the ultrafiltration.

Table 41

Evaluation of Precure Resistance for Lignin RS4-PF-Ammonium Sulfate (4.5%) Adhesive

Adhesive type	Visual evaluation of face after 2 hour boil	IB (MPa)
RS4-PF 30%-70%	Some surface flaking	0.491
BD802	Severe surface flaking	0.411

The preparation of the alkaline solution from the ethyl acetate-extracted lignin highlighted one of the problems with the lignin recovery method used. Method 2, which includes heating of the acidified lignin extract, leads to the production of alkali-insoluble material. The molecular weight distributions and properties of the lignins recovered after ultrafiltration are affected by the recovery process.

The acid precipitable lignins produced by anodic oxidation in basic aqueous media undergo changes involving a decrease in phenyl groups and an increase of the carboxylic groups of the lignins and an opening of benzylic rings.

Characterization of the acetone-solubles recovered after electrolysis indicate drastic changes from the starting lignin. These changes are indicative of the formation of carbonyl carbons in esters or quinoidal structures, but the former interpretation is favored.

The yields of low molecular weight products produced by oxidation with increasing passage of charge indicate that the first formed products are undergoing further reaction.

Attempts to provide a parametric analysis of the electrolysis process were unsuccessful. However, the experiments indicated little production of volatile organic products and limited carbon dioxide production. Analysis of ethyl acetate solubles produced indicated the production of alkanedioic acids. Problems experienced with the analysis of the alkaline electrolysis solutions is an example of the difficulties encountered in analyzing lignin reaction products, and the need for analytical methods development.

Products of oxidation of steam-treated aspenwood lignin using peroxydisulfate, ($S_2O_8^{2-}$-Cu^{II}), in acetic acid are dependent on the available functional groups within the lignin, and can either lead to substantial depolymerization when the available hydroxyl functions are blocked and polymerization when they are available. Only low yields of monomeric products were obtained.

Metalloporphyrin oxidations on lignin were not investigated because of concerns with the observation of trace quantities of chlorinated products, the observation in two cases of oxidation in the absence of metal complex, and that when oxidation occurred only very low conversions were observed and products were dependent on starting material.

The low molecular weight lignin fractions from batch and constant volume ultrafiltration are more reactive for the formulation of lignin-phenolic adhesives than the corresponding higher molecular weight lignin-fractions. The unfractionated aspenwood lignin could be used to replace 10-20 % of a core PF waferboard adhesive and 30-40 % of a face PF waferboard adhesive.

Preparation of a powder, pre-cure resistant surface adhesive for waferboard demonstrated that steam-treated lignin could be used to replace 30% by solid weight of a phenol-formaldehyde in the formulation. The lignin-PF resin had a curing speed similar to a commercial surface phenolic resin.

The sub-contract with Concordia University demonstrated that the steam-treated lignins could be successfully utilized in polyblend formulations with an epoxy (EP) adhesive (Ciba Geigy AY 103-HY 956). When compared with the EP control, the adhesive strength in shear of the EP-20% unfractionated lignin and EP-20% <10K lignin fraction disclosed superior performance, i.e., 15% and 30% higher respectively. The adhesive shear strength of the EP-<10K lignin fraction polyblends at a lignin content superior than 10%, after accelerated weathering is still higher than the EP control. In the same polyblends kraft lignins has little effect on shear strength. In the polyurethane (Desmodur E14-Desmophen 1920D)-lignin sealant systems, the effect of lignin upon the mechanical properties is less obvious than in the EP-L blends.

SECTION II

COST ESTIMATION FOR THE FRACTIONATION AND RECOVERY OF LIGNIN FROM STEAM EXPLODED ASPENWOOD USING ULTRAFILTRATION AND ACID PRECIPITATION METHODS

1.0 INTRODUCTION

Lignin is a by-product from the bioconversion of lignocellulosic material to ethanol. The credit for lignin is very important to the economics of the bioconversion process. One processing option is to extract lignin from steam pretreated lignocellulosics with sodium hydroxide solution. Lignin is then recovered from the caustic extract by acid precipitation. Lignin isolated in this way has a wide molecular weight distribution, and thus has limited application as chemical feedstock. Another method for obtaining lignin products that have narrow molecular weight distributions is to fractionate the caustic extract using ultrafiltration membranes. The fractions are then precipitated separately by acidification. The costs of recovering lignin by the above methods are investigated in this study.

2.0 PROCESS DESCRIPTION

The lignin extraction is common to both methods. Lignin is extracted from water-washed steam exploded wood with dilute sodium hydroxide solution in a counter-current screw-conveyor extractor. To minimize the use of caustic, the extractor is designed such that the lignin concentration in the final extract is near the saturation point.

2.1 LIGNIN RECOVERY BY ACID PRECIPITATION

The schematic diagram of the lignin precipitation process is represented by Figure 40. Lignin extract, coming out of the extractor at 50-60°C, is heated

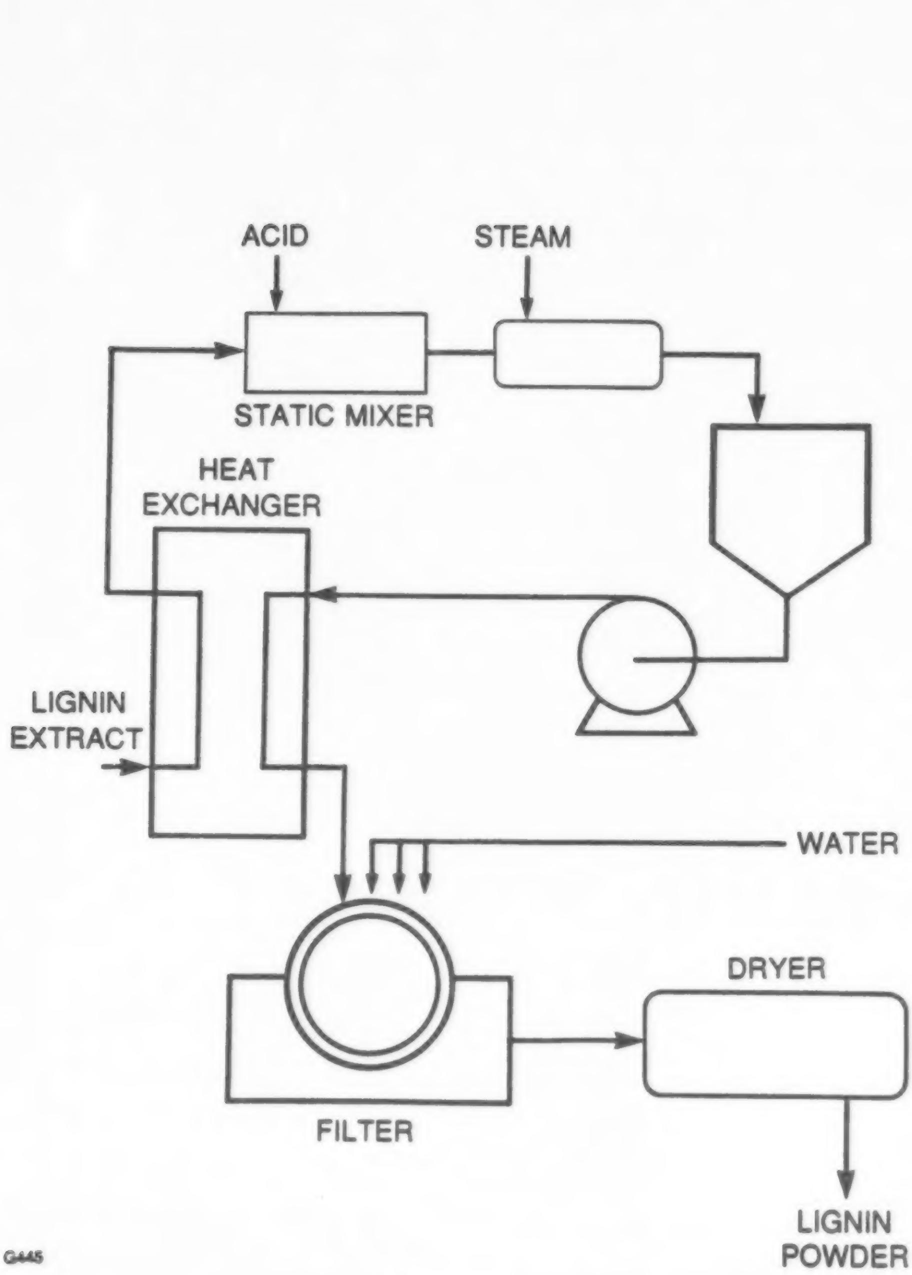
ACID
STEAM
STATIC MIXER
HEAT EXCHANGER
LIGNIN EXTRACT
WATER
DRYER
FILTER
LIGNIN POWDER
G445

Figure 40 Schematic Diagram of Lignin Precipitation Process

to about 80°C in the plate heat exchanger by hot lignin precipitate slurry. The pH of the extract is lowered to 2.5 by adding sulphuric acid. The temperature of the lignin slurry is brought up to 90°C by direct steam injection. The hot slurry is held in a surge tank for about 2 hours for the lignin to coagulate before being pumped to a vacuum drum filter where the lignin is separated and washed with water. The lignin cake is dried to 95% solid in a drum dryer.

2.2 LIGNIN FRACTIONATION BY ULTRAFILTRATION AND ACID PRECIPITATION

The lignin extract is fractionated into three fractions by ultrafiltration (UF) modules as shown in Figure 41. Insoluble particles in the extract are removed by the micro-filter. This is a multiple-cartridge filtration unit with automatic backwash. The temperature of the extract fed to the UF units is controlled at 60°C. The primary function of the UF system is to fractionate the lignin and not to recover the caustic. Because the dissolved lignin concentration is near the saturation point, any attempt to recover the caustic may cause lignin to drop out of solution and plug up the membranes. The lignin separation is achieved by selecting different pore sizes of the membranes and by controlling the recycle rates. Each lignin fraction is then forwarded to a separate acid precipitation system similar to the one described in the previous section. In this case study there are three separate acid precipitation systems, one for each lignin fraction.

3.0 SPREADSHEET MODEL

The material balance and cost calculations are formulated into a Lotus 123

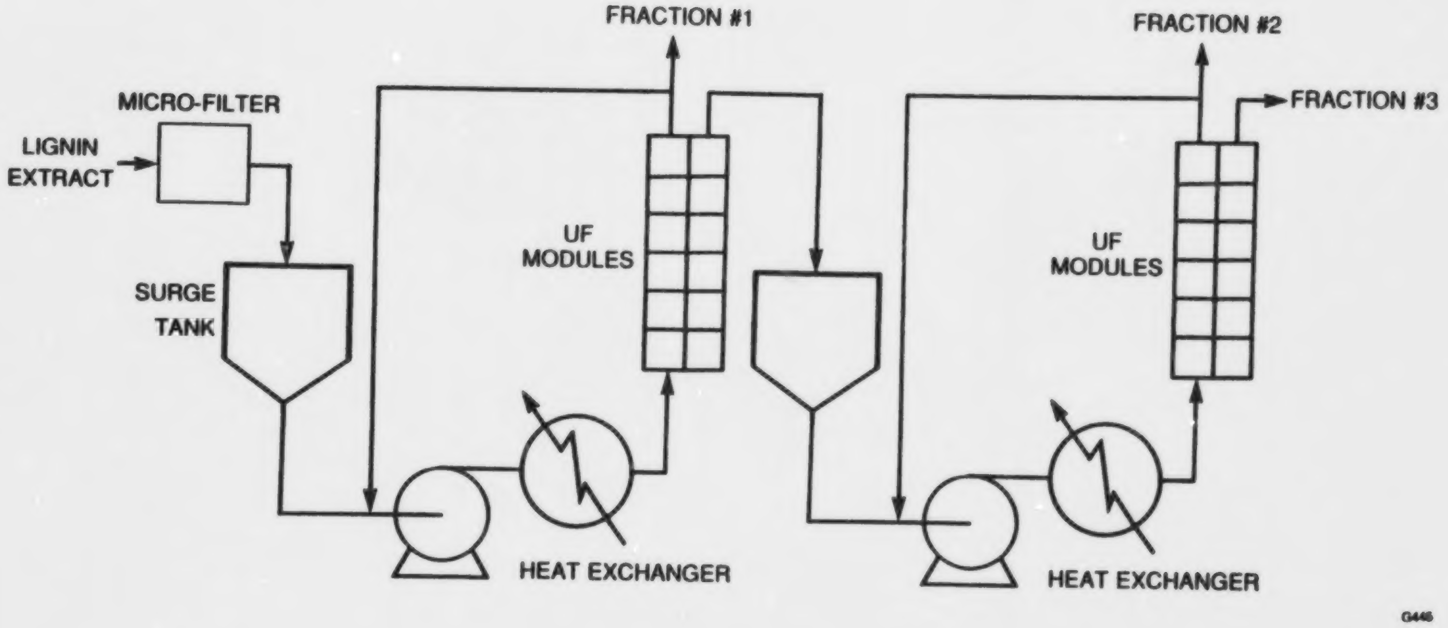
FRACTION #1
FRACTION #2
FRACTION #3
MICRO-FILTER
LIGNIN EXTRACT
SURGE TANK
UF MODULES
UF MODULES
HEAT EXCHANGER
HEAT EXCHANGER
G446

Figure 41 Schematic Diagram of Lignin Fractionation by Ultrafiltration

spreadsheet model. The model consists of the following main parts.

3.1 PROCESS AND ECONOMICS VARIABLES

Important parameters such as lignin recovery yields, lignin concentration, caustic concentration, ultrafiltration flux, chemical costs, etc., form the input variables of the model. For the base case, values of these parameters are based on laboratory results and best available technology (Table 42). These values can be changed to effect variation in the cost of lignin.

3.2 MATERIAL AND ENERGY BALANCE

The material and energy balance determines the equipment sizes and energy requirements. The lignin precipitation process is better defined than the fractionation of lignin using ultrafiltration. Because of lack of pilot plant data, ultrafiltration flux rates of caustic lignin extract are assumed to be similar to those for Kraft black liquor. The final lignin recovery yield for the ultrafiltration method is expected to be slightly lowered than that of straight acid precipitation method because of additional loss via the fractionation process.

3.3 COST ESTIMATION

The cost estimation includes fixed capital cost and operating cost. Fixed capital cost includes purchase cost of equipment, installation cost, contractor's fees, contingency, and capital cost recovery. The capital recovery cost takes into account the costs of equity, long-term debt, taxes, depreciation, and inflation, see Appendix 4.3. The operating cost includes

Table 42

Input Variables for the Lignin Recovery Model

BASE CASE
BASIS: 500 tonnes/day bioconversion plant

NOTATION	VALUE[a]	DESCRIPTION
PROCESS VARIABLES		
INPUT	500	Original wood input, tonnes/day
CNaOH	0.4	NaOH conc. in fresh caustic solution, wt%
fLX	21	Total caustic soluble, wt% of original wood
cLX	4	Total dissolved lignin extract, wt%
YLPPT	80	Lignin precipitate yield, % of total dissolved solids in extract
MCLCAKE	50	Moisture content of filtered lignin, wt%
FLUX	40	Average flux of ultrafiltration system, $L/m^2.h$
HMW	0.4	High MW fraction
IMW	0.3	Intermediate MW fraction
CFHMW	3	Concentration factor for high MW fraction
CFIMW	2	Concentration factor for intermediate MW fraction
UFRF	0.98	Solid recovery from ultrafiltration, %
ECONOMIC VARIABLES		
UCNaOH	0.42	Unit cost of 50 wt% caustic soda, $/kg
UCH_2SO_4	0.14	Unit cost technical grade H_2SO_4 (93 wt%), $/kg
UCSTM	5	Unit cost of steam, $/GJ
UCE	0.04	Cost of electricity, $/kWh
LIFE	15	Depreciation period, year
LTDEBTR	0.3	Long term debt fraction of fixed capital
LTDEBTC	12	Interest paid on long term debt, %
STOCKC	15	Before-tax rate of return of common stock, %
TAX	45	Income taxes, %
PTI	2	Property tax and insurance, % of fixed capital
WCAP	10	Annual working capital, % of fixed capital
INFLA	6	Annual inflation, %
WCROI	25	Before-tax rate of return on working capital, %
FCR	18.3	Fixed capital recovery rate, %

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[a] Selected from this report and literature values: Drouin and Derochers, 1988; Gruthie, 1969; Hall *et al.*, 1982; Nguyen, 1990; Peters and Timmerhaus, 1968; Uloth and Wearing, 1989; Ulrich, 1984.

cost of chemicals, energy and labour. The unit cost of production of lignin is obtained by dividing the sum of capital recovery cost and operating cost by the production rate.

3.4 SENSITIVITY ANALYSIS

Because of the uncertainty in the values on the input parameters, sensitivity is normally performed in the process economic evaluation. The sensitivity analysis is used to rank the economic importance of input parameters. A base case, with a set of specific values for various technical and economic parameters, is established as a standard in sensitivity analysis. The values of these parameters are based on current technology and conditions.

4.0 RESULTS AND DISCUSSION

4.1 COMPARISON OF COSTS OF PRODUCTIONS

The unit production costs of lignin product for the acid precipitation method and for the ultrafiltration method are summarized in Table 43. For the ultrafiltration process, the lignin cost is the average value for the three fractions. The total unit production cost for lignin isolated by acid precipitation process is 12 cents/kg. The cost of caustic soda and sulphuric acid contributes to 58% of total cost. Fixed capital recovery cost contributes only 11% to the total cost.

For the ultrafiltration process the average unit production cost is 17.5

Table 43

Summary of Costs of Production

BASE CASE:	Wood input:	500 t/d
	Lignin production	84 t/d

ACID PRECIPITATION ONLY

VARIABLE COST	$/kg lignin
Chemicals	0.069
Steam + electricity	0.031
Labour	0.007
FIXED CAPITAL	
$2,105,457	0.013
TOTAL	0.120

ULTRAFILTRATION AND ACID PRECIPITATION

VARIABLE COST	$/kg lignin
Chemicals + UF membranes	0.085
Steam + electricity	0.034
Labour	0.014
FIXED CAPITAL	
$6,940,235	0.042
TOTAL	0.175

cents/kg, 62% higher than the cost of acid precipitated lignin. Again, the cost of chemicals contributes the largest fraction (49%) of the total production cost. The fixed capital recovery cost, however, increases substantially to 24% of the total production cost. The total capital investment is more than triple that required for the acid precipitation process. The reason for the high capital cost for the ultrafiltration is the high cost of the ultrafiltration system and each lignin fraction requires separate acid precipitation and drying units.

4.2 SENSITIVITY ANALYSIS

Sensitivity analysis of important process parameters is performed by changing the value of each parameter one at a time and calculating the corresponding production cost of lignin.

4.2.1 Effect of Lignin Concentration in Caustic Extract

As the cost of caustic required to extract the lignin contributes to a major portion of the total production cost it is important to keep the ratio of caustic to lignin as low as possible. Since the solubility of lignin increases with temperature, the extraction should be carried out high temperature. The effect of the lignin concentration in the extract on the production cost is shown in Figure 42. (Tabulations of results for sensitivity analyses are given in Appendix 4.4). To minimize the cost of chemicals the lignin concentration above 3% must be obtained. This can be achieved by using a counter-current extraction process.

4.2.2 Effect of Caustic Concentration

Since the cost of caustic contributes to the largest portion of the total

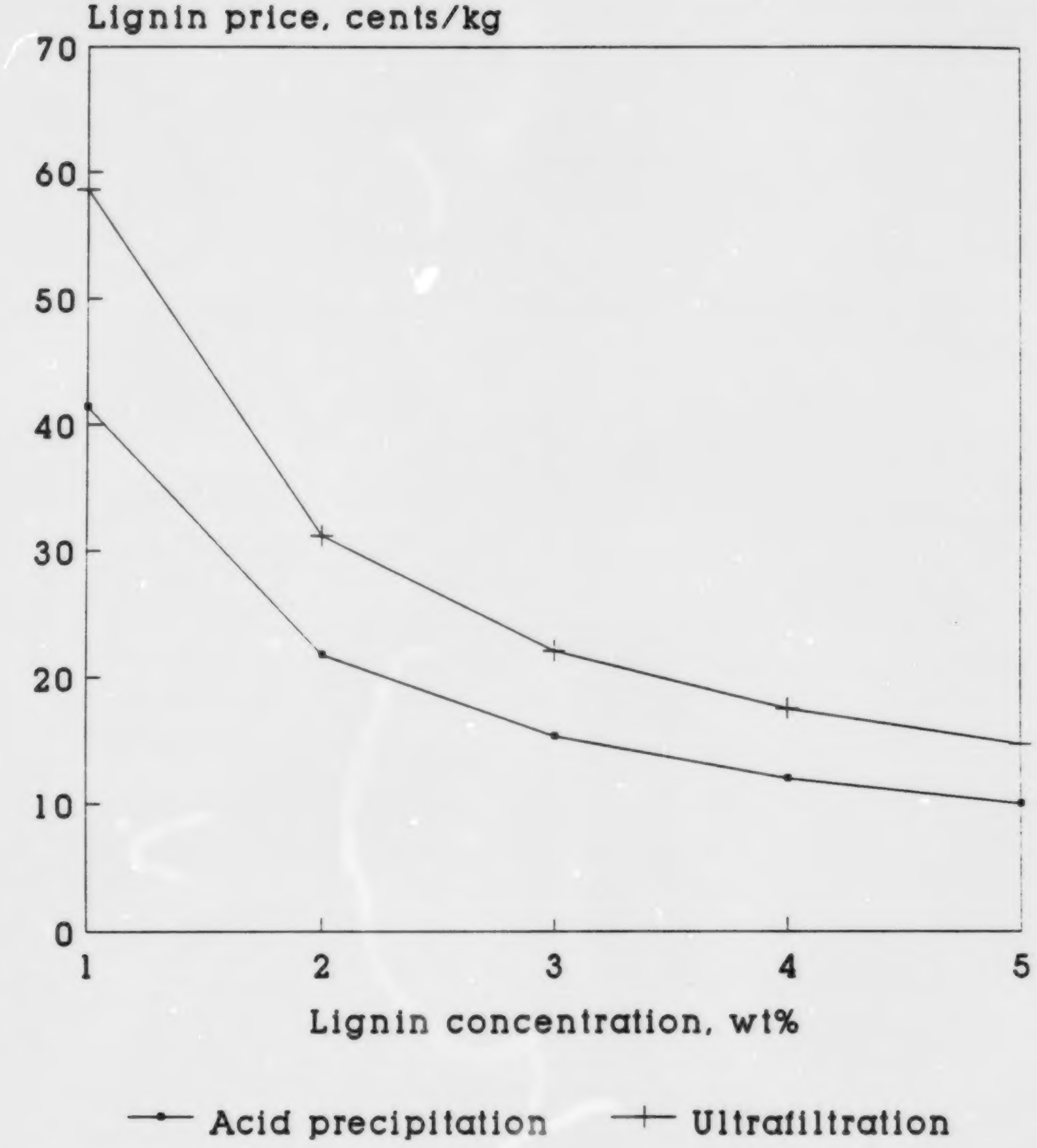

Figure 42 Effect of Lignin Concentration in Caustic Extract

production cost, the quantity of caustic used in the lignin extraction has a significant effect on the final price of lignin (Figure 43). In general, a dilute caustic solution should be used to minimize cost. However, the caustic concentration must be high enough to dissolve the lignin and hold it in solution. The fractionation of the lignin extract using ultrafiltration would likely require higher caustic concentration to prevent lignin from dropping out of solution as each retentate fraction is concentrated by the membrane.

4.2.3 Effect of Lignin Recovery Yield from Acid Precipitation

The lignin recovery yield from the acid precipitation step has a significant effect on the unit price of lignin (Figure 44). The lower the pH the higher the precipitate yield. A pH 2 is assumed in the base case study. Proper control of temperature and retention time is important in obtaining an easily filterable lignin slurry that results in a high recovery yield.

4.2.4 Effect of Ultrafiltration Flux

The ultrafiltration flux rates have a direct impact on the required membrane areas, and thus fixed cost. The flux is expected to reduce gradually with filtration time as the membrane becomes fouled. In the design calculation, it is assumed that the ultrafiltration system is constructed in modules having multiple cartridges or cell units. Each cell unit is automatically back washed when it becomes fouled. To simplify calculation an average flux rate is assumed for the whole system. As shown in Figure 45, the effect of flux rate has only a moderate impact on the cost of production.

4.2.5 Effect of Moisture Content of Lignin Cake

The higher the moisture content of lignin cake from the filter the higher the energy required to dry the final product. The effect of

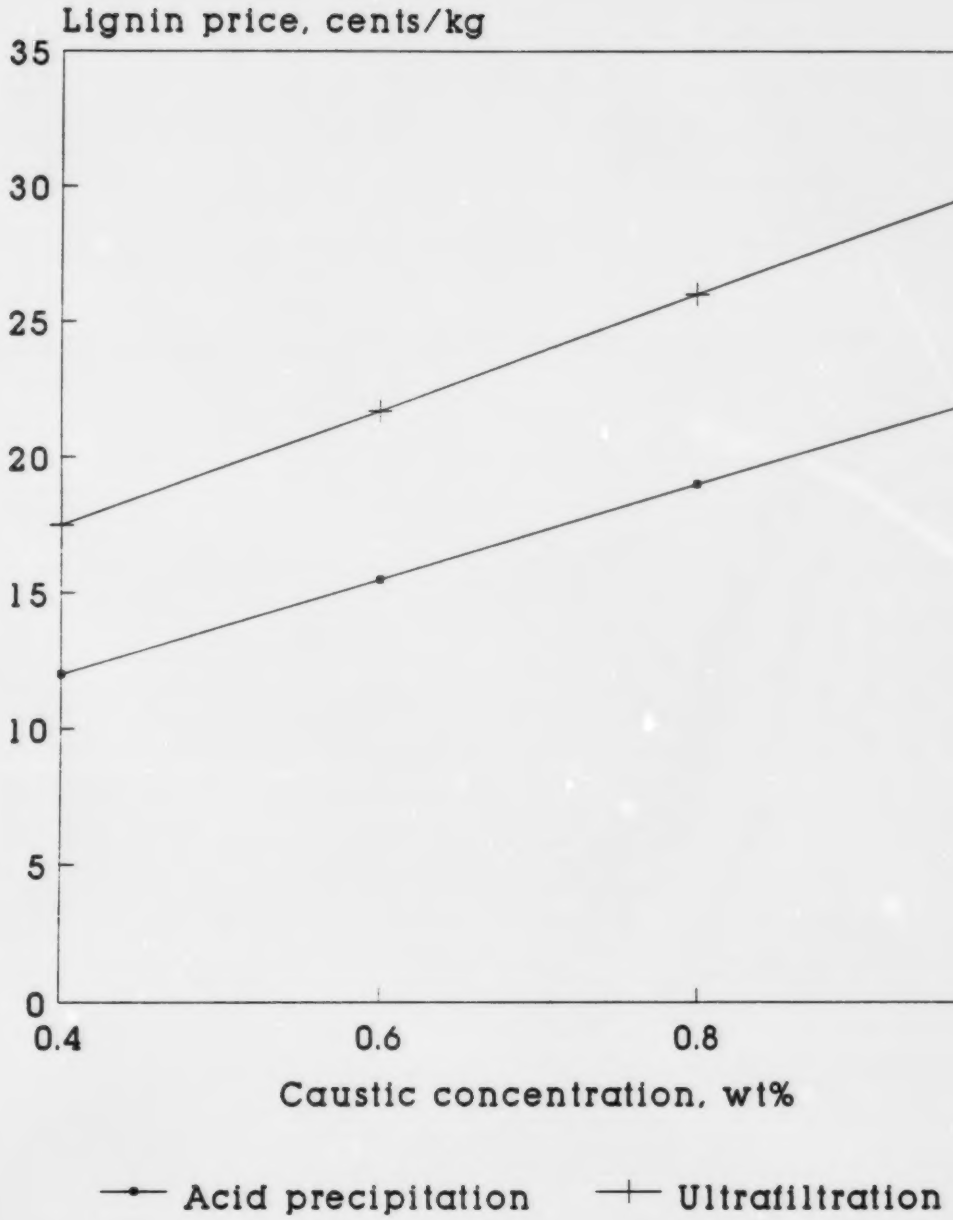

Figure 43 Effect of Caustic Concentration

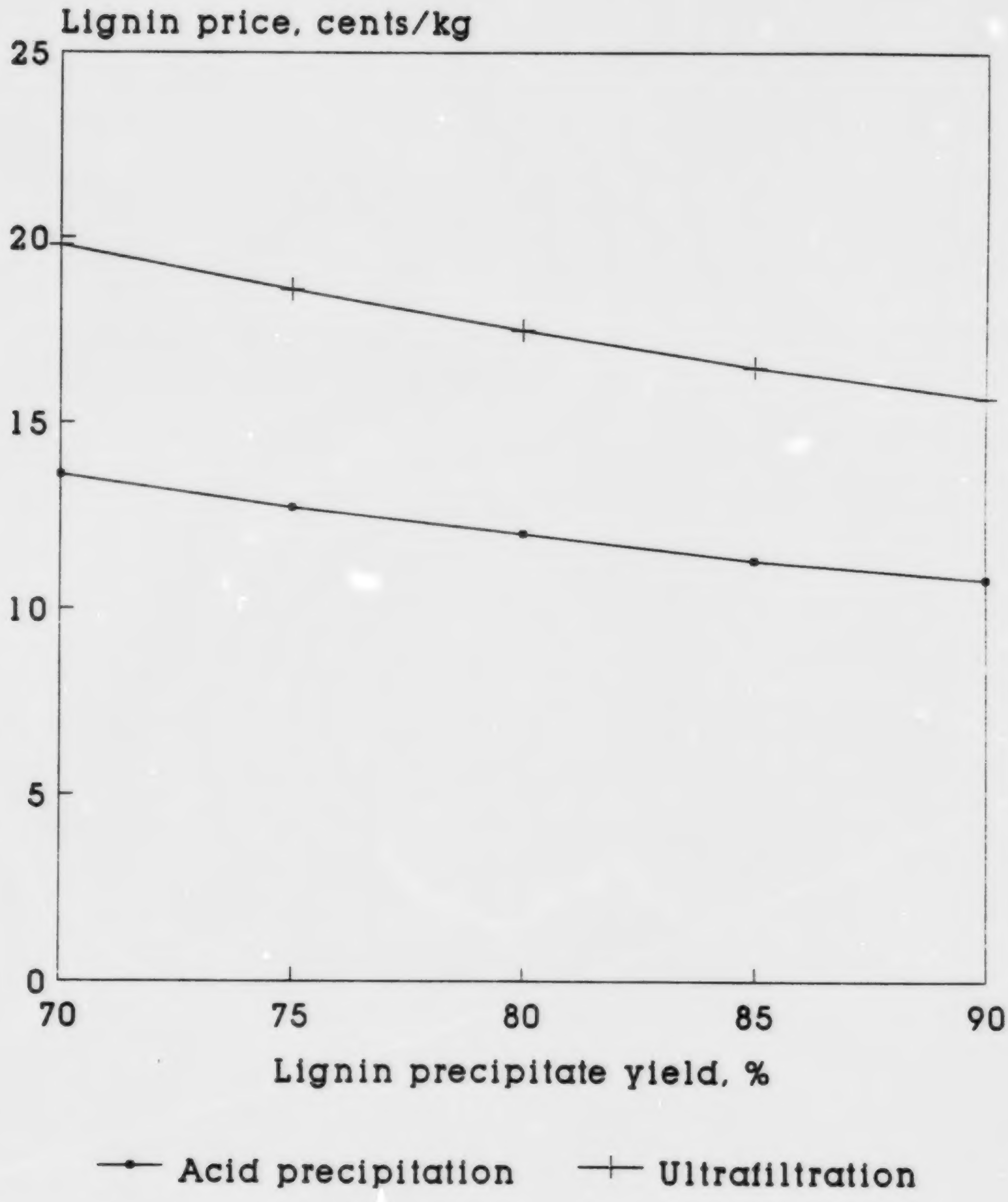

Figure 44 Effect of Lignin Recovery Yield

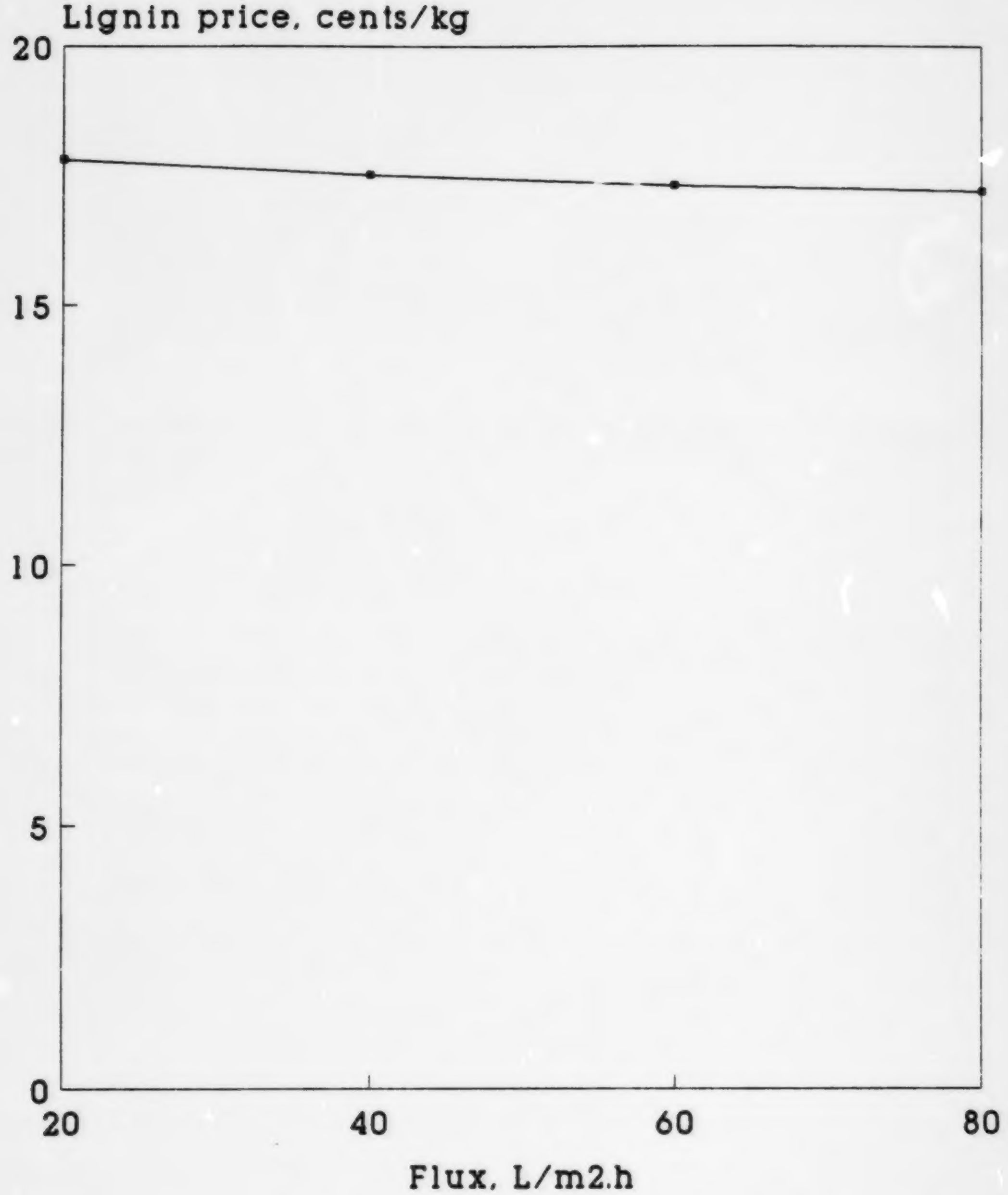

Figure 45 Effect of Ultrafiltration Flux

moisture content of lignin cake on production cost is presented in Figure 46.

5.0 CONCLUSION

The cost of fractionation of lignin using ultrafiltration followed by acid precipitation is estimated to be 17.5 cents/kg. This is 62% higher than the cost of lignin recovered by acid precipitation alone, which is estimated at 12 cents/kg.

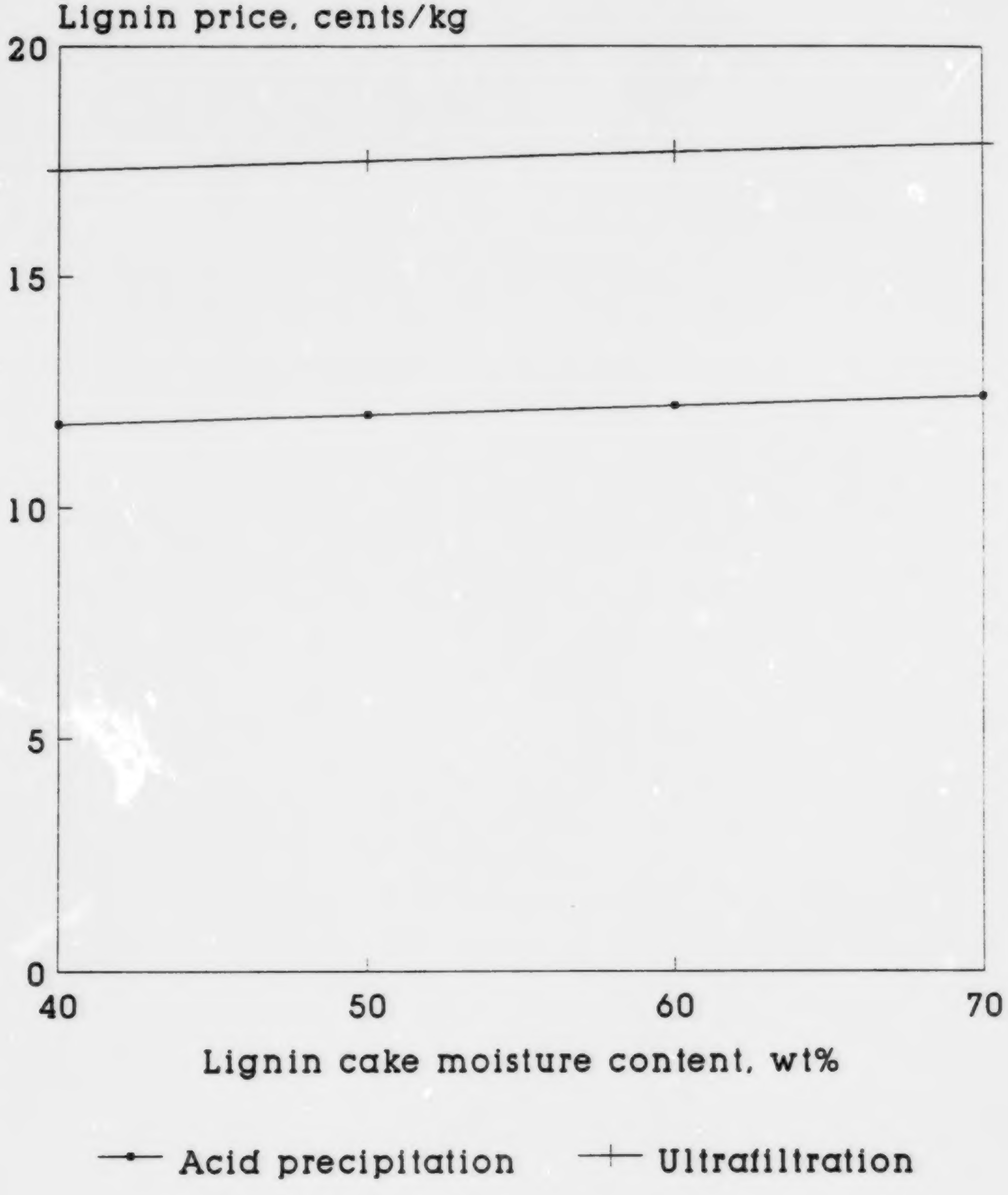

Figure 46 Effect of Lignin Cake Moisture Content

SECTION III

ECONOMIC ANALYSIS OF LIGNIN USE IN WOOD PRODUCTS ADHESIVES AND AS FUEL OCTANE ENHANCERS

1.0 INTRODUCTION

The objective of this economic analysis is to determine whether and under what circumstances:

- the lignin fractions produced as a co-product of bioconversion processes will meet with market acceptance as a phenol substitute in adhesives used by the panel products industry, and,

- the methyl aryl ethers produced from conversion of these lignin fractions will meet with market acceptance as octane enhancers in fuels.

To achieve the research objective, our analysis focussed on end use markets in order to assess the key determinants of demand for the lignin fractions/substitutes in the two applications. In the case of the wood products industry, the critical end use market is comprised of the panel manufacturers.

In evaluating the potential for lignin in the octane enhancement application, we initially assumed the critical end use market would be fuel refiners. However, our research revealed that the refiners were more appropriately viewed as intermediaries responding to the needs of the automotive manufacturers for specific types of fuels to power the vehicles they produced.

Most importantly, our research revealed that in both applications, perhaps the most significant determinants of future demand for the lignin fractions would be environmental protection regulatory initiatives. These initiatives could influence the fundamental direction of development of wood products adhesives and automotive fuels and therefore will likely affect demand for the lignin fractions under consideration in this analysis. Both these public policy areas will be discussed below in more detail, within the context of the market assessment for each product.

In each of these applications, lignocellulosics have been used as a derivative source for the compounds for many years. Therefore, the adhesives manufacturers and the panel producers have had experience using lignin-based substitutes for phenol in adhesive resins. As well, fuel refiners and blenders have had extensive experience with biomass derived octane enhancers.

Our analysis showed, however, that this experience could be equally an advantage or a disadvantage in evaluating the likely market acceptance of the test compounds. The advantage was that manufacturers readily accepted the concept that substitutes for existing compounds could be derived from lignin. Therefore, it was not necessary to explain new technology or to engage in a persuasion process prior to evaluating the potential market acceptance of the test product.

The disadvantage was that manufacturers were highly sceptical that a new formulation could overcome deficiencies they had found to exist in previously tried products. The result was that those interviewed invariably adopted the position '*tell me how a new product could be better and different than what I've seen before, and tell me what it will cost, and I'll tell you if I'm interested in trying it*'! A product definition that would have been appropriate to that type of response was not contemplated within the scope of this research project. Therefore, a conventional market analysis, with an objective of estimating future demand scenarios for a product, was deemed to be unrealistic and likely to be unproductive.

The focus of the market evaluation research we did undertake therefore shifted to identification and evaluation of the basic determinants of demand in the market for each lignin fraction -- adhesives and fuel additives.

The analyses of the two market areas yielded one common raw material issue to be addressed before significant market acceptance could be achieved. The analyses also identified a number of very different research and product development issues which must be addressed. While it is possible to group some of these latter issues together for analysis, the differences suggest separate treatment of the two markets will be more productive. Therefore, the remaining sections of this chapter will focus first on the common raw material issues and then, subsequently, will report on the analyses of each market separately. Some conclusions will be drawn at the end.

2.0 LIGNIN AND RAW MATERIAL/RESOURCE SUPPLY ISSUES

Over the past two decades there has been much research into the potential use of refined lignin in both adhesives and fuels. Among the primary motivations for that work was the concern that future shortages and/or significantly increased costs of the petrochemical-derived substances then (and now) in use would force users of the two products to consider substances derived from alternative, renewable sources.

During the same period, forest resource managers in North America began to shift from their then prevalent view of the substantial volumes of under- or unutilized aspen-poplar as a weed species of little or no value, to consider it as a resource for which some use should be found.

These two factors combined to spur at least three major thrusts of research activity:

- investigation of the potential for using the poplar resource as furnish for a number of different pulping technologies, notably the thermo-mechanical and the newer chemical-thermo-mechanical technologies;

- assessment of the potential for refining the resource into fuels or related substances; and,

- evaluation of the opportunities to use these species in solid and converted wood applications, including panel products.

Each of these areas of research has yielded some specific results.

Aspen-poplar is now used frequently as a pulp furnish, the technical feasibility of refining the round wood into fuels is well established, and solid wood products markets, especially in Europe, are growing particularly in the areas of cut-to-size furniture stock and packaging grades. The net result is that North American demand for aspen-poplar round wood has grown substantially over the past two decades.

These developments are important for the economic analysis research related to the adhesives and fuels applications of lignin.

The theoretical economic analyses related to these research efforts (Chum *et al.*, 1985c; Howatson, 1986; Bergeron and Hinman, 1990; Sellers, 1990) have used estimated lignin production costs derived from a pre-treatment process separating the cellulose, hemi-cellulose, lignin and furfural. This process itself is described most fully by Chum *et al.* (1985c).

There are two basic values cited in these research papers.

These are the estimated fuel value of lignin as approximately $44.00/ton; and, the estimated production cost of lignin as approximately $22.00/ton or $32.00/ton, depending on the separation process used.

These production cost estimates were calculated by Chum *et al.* (1985c) and assumed that all feedstock costs are allocated to cellulose production. That is, no raw material feedstock costs were allocated to the production of hemi-cellulose, lignin or furfural.

If feedstock costs had been allocated on a weighted value basis across the production of cellulose, hemi-cellulose, lignin and furfural, the production costs of lignin would increase to $88.00/ton from the organosolv process and to $68.00/ton for the steam explosion process. This would suggest that the estimated lignin selling prices derived from the Chum model would increase from the cited level of $28.00/ton to $94.00/ton for the organosolv process, and from the cited level of $40.00/ton to $72.00/ton for the steam explosion process.

In the Chum model, feedstock costs represent 38.7% of total production costs in the case of the organosolv process and 46.6% of total production costs in the steam explosion process. Therefore, the Chum analysis suggests that feedstock costs of $ 34.00/ton would be required for the organosolv process to be viable, and that feedstock costs of $31.69/ton would be required for the steam explosion process to be viable. These values are, incidentally, also similar to the assumed feedstock values of $30.00/ton used by Elliott *et al.* (1990).

However, these cost levels are low relative to costs incurred by other aspen-poplar using industries across North America. A study commissioned by Ontario's Office of the Restructuring Commissioner in 1988 (CPM Consultants,

1989) showed that waferboard mills in North America typically paid $40.00/ton -- $48.00/ton for aspen-poplar. Only in those regions where there was no other competing demand on the available total timber resource, (from a pulp and paper mills for example), did the wood costs for aspen using mills decrease to the $30.00/ton -- $36.00/ton range.

It seems unlikely therefore, that the feedstock cost levels assumed in the theoretical could be achieved in an operating industrial environment.

The traditional source of lignin supply, particularly for further refining as an adhesive component, has been as an extract from the black liquor produced in pulping. If demand for lignin grows significantly, it will be because uses for it can be found that generate values greater than its fuel value -- which is widely accepted by researchers as 2.2¢/lb. or $44.00/ton (Chum *et al.*, 1985c; Lönner and Törnqvist, 1990). If such new uses are developed, diversion of lignin from current use as fuel in the pulping process could occur.

It has been noted (for example: Chum *et al.*, 1985c; Lönner and Törnqvist, 1990) that modern pulp mills are sufficiently energy efficient that lignin surpluses, (to fuel requirements), are generated. This begs the question of whether this scenario is realistic, given that relatively little of the installed base of pulping capacity in North America would fall into this modern *category*. As well, it is unclear whether the suggested diversion of lignin would cause other shifts in energy demand patterns in the pulp industry, such as increased use of electricity.

Such shifts, if they were to occur, might be directly counter to the intent of public policy in some jurisdictions, where there is an explicit desire to reduce such industrial demand for electricity.

The research cited previously which deals with use of lignin as either a fuel source or as an adhesive component makes implicit assumptions that sufficient wood supply for the proposed process/application under consideration will be available at the price levels that are assumed or derived from the analyses as necessary to the viability of the process.

These assumptions may have been valid in the early 70's, when there was very little demand on the available aspen-poplar timber resource. However, the industry analyses cited above clearly show that there is considerable and growing demand for this timber species. For example, waferboard/OSB was first produced in Canada in the mid-70's, and today there are some 16 mills producing 100 Million panels annually, drawing almost exclusively on the aspen/poplar resource for raw material. As well, kraft pulping technology and the newer thermo-mechanical pulps today draw extensively on the aspen/poplar resource.

Differences in harvesting procedures, land tenure and allocation policies, stumpage regimes and, as noted previously, competition for the available timber resource create significant variations in delivered wood costs (Trusty, 1989; CPM Consultants, 1989), across the country, and even within regions. These variations are likely to have a significant impact on the cost and availability of raw material for processing into lignin, as well as on the cost/value of lignin derived from pulping processes.

These changing usage patterns would suggest that the potential supply of both aspen/poplar for processing into lignin and, therefore, of lignin itself is considerably more problematic than most of the available literature and research would suggest.

Therefore, it is suggested that additional detailed research is warranted in order to evaluate properly the following issues related to the supply and cost of raw material for the lignin processes under consideration:

- Are the round wood prices, derived from the models, and apparently necessary to the viability of the processes under consideration, accurate; and, more importantly, are these price levels realistically achievable? If so, in which areas of the country or on the continent?

- The conversion processes considered produce lignin as a co-product to enhance the viability of the primary conversion, biomass liquefaction. The analyses also implicitly assume that roundwood will be available in sufficient and very large quantities to supply the processing mills. Are the supply assumptions on which these analyses and models have been developed valid? What is the realistic wood supply base that can be drawn upon for these processes, and, can that supply be maintained over the long term?

- What are the comparative added values that can be derived from the available timber supply base by converting to pulp and paper, solid wood products, converted wood products, fuels and fuel additives, and adhesives?

- What is the comparative value of lignin used as an energy source in pulp mills to other values that can be derived from the same raw material supply? And, what is the comparative value of lignin as a pulp mill energy source to other forms of substitute energy?

- What will be the impact on demand for the aspen/poplar resource of substantial growth in the use of lignin? Is it realistic to expect that use of aspen/poplar for production of lignin will be able to compete on raw material costs with other uses of that species if solid wood or pulp/paper applications continue to grow, as seems very likely?

It is suggested that these issues should be fully evaluated to determine the impact of potential raw material availability constraints on the viability of the refining processes and applications discussed in this study.

3.0 PHENOL SUBSTITUTION IN FORMALDEHYDE ADHESIVES

3.1 CURRENT MARKET -- PHENOL-FORMALDEHYDE ADHESIVES

Several observations are important as a preface to the analysis of the market for phenol-formaldehyde (PF) adhesive resins. These are:

- The major market for PF resins is in the manufacture of structural panel board products, (softwood plywood, hardwood plywood, waferboard and oriented strand board [OSB]), which are used primarily in North American construction of residential and small commercial buildings. The market for PF resins is therefore ultimately driven by such macro economic factors as interest rates, economic growth, and employment, which in turn determine the level of housing starts.

- The panelboard market is continental in scope and the demographic structure of the North American population is therefore an important factor in determining overall demand for housing. It is important to note in this regard that, in aggregate terms, the maturing of the baby-boom population node has brought about the beginning of a projected long term decline in the growth rate of household formation and, consequently, of continent-wide demand for housing. Therefore, the level of housing starts in North America can be expected to decline for the foreseeable future and, as a result, North American demand for commodity building materials, such as structural panels, will similarly decline. [A significant policy shift with regards to permitted levels of immigration by either the American of the Canadian Governments could change this forecast.]

- Waferboard/OSB is expected to continue to displace plywood in sheathing uses in construction, and some further displacement of solid boards by panels will occur. Therefore, there may be relatively higher growth in demand for waferboard/OSB over the balance of the decade than is likely to be the case for other structural panels. Notwithstanding that potential growth, the longer term viability of a number of Canadian panelboard mills is questionable, particularly as many of these mills are older and smaller by current industry standards.

- Because of their use in construction applications, and their competitive position vis à vis other construction materials, the market for panel boards is a commodity market. Therefore, by extension, the major manufacturing inputs, including resins, must be viewed as commodity products as well. As is the situation in virtually all such markets, price is the overwhelmingly important determinant of marketplace success. To be successful, a lignin substitute for phenol must therefore offer the resin manufacturer tangible, achievable and realistic production cost savings.

In Canada, resin costs represent 15% - 18% of the total production costs for waferboard/OSB, at a current estimated average cost of $0.75 -- $0.80/lb. At full capacity this represents a total industry expenditure on resins of approximately $100 Million annually. In the United States, waferboard producers incur similar unit costs, though total resin costs represent a higher proportion of total manufacturing costs because of relatively lower wood costs.

3.2 PANEL BOARD RESINS -- EXPERIENCE WITH LIGNIN

The Canadian panel boards industry annually consumes some 93,000 tonnes of Urea Formaldehyde, (UF), resins, with a current value of approximately $60 Million, and some 50,000 tonnes of Phenol-Formaldehyde, (PF), resins with a current value of approximately $90 Million. The UF resins are used primarily in the non-structural panels which are used primarily in interior and furniture component applications. The primary type of panel in this category is particleboard, with some use being made of plywood and medium density fibreboard, (MDF).

The PF resins are used primarily in structural panels, both interior and exterior uses. The basic reason for this is that the bond provided by the PF reaction in the panel pressing process will withstand the strength and durability requirements of structural and exterior use, a result that cannot be achieved by UF resins. The primary types of panels in this category are waferboard/oriented strand board, (OSB), and plywood. The production of hardboard, while limited, also uses PF resins.

Lignin has been tried as substitute for phenol in the PF resins since the early 70's. Industry personnel interviewed for this study reported that there have been several problems experienced with lignin usage. These include:

- inconsistency in resin bonding, resulting in instability in panel dimensions, especially thickness, and,

- inconsistent shearing of the powder resin with the other compounds which creates difficulty in achieving a consistent distribution of adhesive throughout and across the panel.

The net effect of these problems is that the panel manufacturers have not yet experienced a lignin substitute that results in a reliably stable panel product. A number of companies are reported to have research underway to address these specific deficiencies; however, panel manufacturers interviewed for this project expressed a very high level of scepticism that solutions could be found in the near term. Nevertheless, there was some consensus that solutions would likely be developed eventually.

It was also noted by panel industry officials that the problems described were encountered at the mill level in a production environment, even though they had not been identified in laboratory testing. Some other respondents also suggested that some of these difficulties could be mill or production line specific.

Panel industry respondents also reported that use of lignin as a phenol substitute did not result in cost savings that had been promised by the lignin substitute promoters. Further, it was suggested by a number of respondents that such savings were unlikely to be achieved because phenol is itself a low-priced commodity product and it is highly unlikely that lignin can ever achieve competitive price levels. Only if the price of oil were projected to increase dramatically or if a significant technological breakthrough was achieved in the processing of lignin, were respondents prepared to agree that lignin could become a cost-effective substitute for phenol. It should perhaps be noted that these views may reflect the relatively low oil prices which prevail currently.

Nonetheless, nearly all respondents in the panel industry noted that their need for production cost savings, however these might be achieved, would always result in some industry interest in future developments of resin products.

Industry experience with deficiencies in lignin-formaldehyde resin at the production test stage also led several respondents to suggest quite strongly that further research, if undertaken, should be proven successful at the pilot plant level, before production environment testing is attempted. The comment was offerred that past experience with moving from the laboratory directly to testing in a production environment had not proved successful or productive, and that further testing at the pilot plant level would be more likely to uncover the deficiencies experienced in the plant, without causing the panel manufacturers to incur the costs related to that experimentation.

3.3 PANEL BOARD RESINS -- NEW ISSUES & SIGNIFICANT CHANGE

Perhaps the most critical issue affecting the future potential for lignin as a phenol substitute in resin production is unrelated to its performance as a resin compound. That issue is the potential impact of possible further restriction and regulation of formaldehyde emissions resulting from the production of panelboards. Specifically, our research uncovered significant and increasing concern that several Canadian jurisdictions may be about to adopt lower in-plant emission standards and/or lower atmospheric emission standards that might not be achievable by the waferboard/OSB manufacturers.

Our research confirmed that the Canadian Federal Government as well as a number of provincial Governments are evaluating whether currently permitted levels of formaldehyde emissions in or from manufacturing facilities and processes are appropriate. While at this writing, it is premature to forecast with any certainty the standards which are likely to be imposed on the panel manufacturers, several Government and industry officials interviewed accepted the likelihood of further reductions in allowable emission levels.

Waferboard/OSB industry respondents have indicated that they believe existing plants may be able to meet somewhat reduced emission standards while continuing to use formaldehyde-based resins. However, achieving that level is expected to require significant investment in sophisticated ventilation and filtration equipment, the capital cost of which has not yet been determined. It was also noted by one industry official that it will be virtually impossible for particleboard manufacturers to meet the proposed standard without substitution of the formaldehyde resins currently in use.

However, it was suggested by several respondents that adoption of the most stringent levels of allowable formaldehyde emissions could probaly not be met by most existing mills, without significant changes to existing production technologies, including resin formulaltions.

In considering this issue, it must be remembered that Canada's panelboard manufacturing plants can be generally characterised as older. In many cases, these mills are only marginally competitive today, and a requirement to invest in emission control equipment that does not yield some offsetting productivity gain will likely render them uncompetitive.

Therefore, the need to investigate and develop alternatives to formaldehyde-based resins can be seen as potentially essential to the survival of much of the Canadian wood panel manufacturing industry.

Isocyanate adhesives have been mentioned in industry analysis literature (CPM

Consultants, 1989) as a possible substitute for formaldehyde resins. However, that research indicates and industry respondents corroborate that much research remains to be done before these adhesives will perform with the reliability and stability that would permit their full and easy substitution for PF resins. Some respondents observed that performance deficiencies of the isocyanate adhesives may be a function of the technological level of the presses in which the trials were conducted. This may therefore suggest an area for further investigation.

4.0 OCTANE ENHANCER/FUEL PRODUCTION FROM LIGNIN

4.1 BACKGROUND -- LIGNIN USE AS A FUEL OR FUEL ADDITIVE

Much of the recent economic analysis of the potential use of lignin refined from direct biomass liquefaction has focussed on process issues (see for example: Chum *et al.*, 1985c; Bergeron amd Hinman, 1990; Graham, 1990; Lönner and Törnqvist, 1990). Specifically, the objective of this work has been the evaluation, at the laboratory level, of the production costs that will likely result from the different processes being considered.

From the research findings, and from interviews with industry personnel, it is possible to draw the following conclusions:

- Lignin can be converted into ethyl aryl ether (EAE), or methyl aryl ether, (MAE). These alkyl aryl ethers will perform effectively as an octane enhancer substitute for toluene/xylenes and ethers such as methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), and methyl tertiary amyl ether

(TAME). In considering lignin-based ethers as a substitute for MTBE, the primary factor on which the ethers have had to be competitive is price. Indeed, this has historically been the case for biomass fuels and fuel additives developed as potential direct substitutes for petroleum-based fuels or for petrochemical-based fuel additives.

In essence, biomass derived fuels and fuel additives developed as potentially competitive substitutes for well established, conventional commodity fuels and fuel additives will be perceived in the marketplace as merely alternative commodities. As such, potential buyers will apply the same purchase criteria to these products as to the conventional products; and, in commodity product markets, the most important of these purchase criteria is almost always price.

For example, Bergeron and Hinman (1990) have examined the cost-competitiveness of MAE compared to MTBE and have found that even when the price of oil is assumed to be $35.00/barrel, the estimated price of MAE only comes to within $0.06/gallon of the market price for toluene/xylenes, as developed within that same analysis.

Therefore, until and unless lignin refined from biomass becomes cost competitive with toluene, the conventional petrochemical feedstocks will not be displaced. Put slightly differently, until oil or natural gas prices increase substantially from prevailing levels, or until the cost of aspen/poplar declines dramatically from current levels, the alkyl aryl ethers will likely remain uncompetitive.

- The process focus of much of the published research has meant that many of the researchers have made assumptions about the availability and cost of raw material supply. As discussed during the first section of this chapter, such assumptions may have been valid during the early 70's, when aspen/poplar was not used in pulping and before waferboard/OSB had been developed as the product we know today.

  However, the demands on the resource base that is assumed to be available for these biomass liquefaction processes have changed dramatically in North America over the past fifteen years. Therefore, it is not at all clear that the availability and cost assumptions that prevail in much of the published research remain valid today. Therefore, as suggested previously, there is an urgent need to test the validity of these assumptions about supply and cost of aspen/poplar. This is particularly important because of the sensitivity of the alkyl aryl ethers to feedstock input costs, and because of the importance of price to the competitiveness of these products in a commodity market.

- If lignin-derived alkyl aryl ethers can be produced and sold at a price level that is competitive with MTBE, potential demand can be assumed to be equal to the current demand for MTBE and any other equivalent octane enhancer.

  This conclusion, however, begs the question of whether use of the potentially available forest resource for biomass liquefaction can compete with other uses to which that resource might be put. As suggested previously, it is therefore, important that research be undertaken to evaluate the comparative values that can be derived from the various uses to which the resource can be put.

4.2 FUEL AND FUEL ADDITIVE MARKETS -- A CHANGING ENVIRONMENT

As described in the preceding sections, current research into the use of lignin-based alkyl aryl ethers as a substitute for petrochemical-based octane enhancers, such as MTBE, can generally be described as being focussed on achieving incremental improvements in production costs, process efficiencies and performance effectiveness. That is, the goals of the researchers seem to be to develop a lignin-based alkyl aryl ether that is a cost-effective substitute for MTBE.

Researchers are attempting to achieve these improvements in the context of using the lignin derivatives in conventional fuel applications. As a result, the target market for the alkyl aryl ethers resulting from the research is the refiners and blenders of transportation fuels, primarily the large oil companies.

Recent developments in environmental policy and regulation, especially in the United States suggest that this focus may not be the most appropriate. A recent special report published in an oil industry journal (Anon, 1990) summarized the issue as follows:

> "The resurgence of environmental awareness in the U.S. could present a refining challenge during the 1990's as great as that of World War II or of unleaded gasoline.
>
> In particular, tougher environmental regulations targetting vehicle emissions will change the nature of the fuels produced by refiners and the processing schemes used to produce the fuels.
>
> By the end of the 1990's, refiners will be formulating gasoline and diesel fuel as much to meet environmental considerations as to meet

> quality requirements.
>
> That could mean substantial changes in refinery process configurations by the end of the decade.
>
> Present and proposed U.S. Environmental Protection Agency, (EPA), rules and pending legislation in the U.S. Congress to reauthorize the Clean Air Act of 1970, call for specific fuel formulas and fuel specifications to improve air quality in the U.S. They may also call for alternate fuels to be marketed in urban areas with the most severe air-quality problems.
>
> Important features of the fuels for the 1990's will include mandated oxygen content and lower aromatics content of gasoline, lower gasoline vapor pressure, and perhaps lower olefins content. Diesel fuels will have lower sulphur and aromatics content."

The main objectives of the new legislation and regulations in the United States are reduced levels of ozone and carbon monoxide and reduced airborne toxic compounds. "Specific vehicle emissions that have been targetted for reduction ...... include: hydrocarbons (evaporative and exhaust), benzene, carbon monoxide (CO), and oxides of nitrogen (NO_x)."(Anon, 1990)

It is also noted in this report that the auto industry "has a big stake in the fuels issue ..... because any new fuels, reformulated gasolines, or alternatives, will have to work in concert with modern emission-control systems". As well, newer fuels will have to provide the same level of driveability as do current fuels; and without causing reduced fuel economy. This latter point is particularly noteworthy because U.S. regulations mandate steadily increasing levels of fuel economy through the 1990's on vehicles sold in that country (Anon, 1990).

These proposed, reduced emission levels have resulted in significant research efforts focussed on the use of MTBE, ETBE, and TAME, as gasoline blending agents that will maintain driveability and performance characteristics while simultaneously meeting the new environmental standards (Unzelman, 1989a,b, 1990a,b). While indicating that additional work must be done to address such problems as volatility, evaporative tendencies, and CO emissions, these research efforts have shown clearly that there is a significant potential role for ethers as fuel additives. The focus of these efforts, however, continues to be on development of fuel and fuel additives that will meet the more stringent emission standards that are to be enforced (see for example: Gibbs, 1989; O'Keefe, 1989; Piel, 1989; Unzelman, 1989a,b, 1990a,b; Anon, 1990; Peyla, 1991).

No similar research efforts based on the alkyl aryl ethers has been identified.

There are two conclusions to draw from this situation that are of particular significance in considering the future potential of lignin-based fuel additives:

- The focus of fuel additive research in the United States is clearly focussed on the need to address impending motor vehicle fuel emission standards, and, as a result, fuel refiners and motor vehicle manufacturers are unlikely to consider using or even testing a fuel additive that does not in some way offer the potential of enhanced emission performance; and,

- The work of the automotive manufacturers to develop advanced fuel combustion technology and emission control systems and to incorporate them into today's motor vehicles has transformed these firms into driving forces in the fuel manufacturing industry. In other words, any research with the objective of developing new fuels or fuel additives should address the emissions control and combustion technology needs of the automotive manufacturers, as much as it addresses the needs of the refiners who would actually be the buyers of the additives.

Finally, unless ethers derived from lignin can meet the new environmental imperatives of reduced emissions while simultaneously maintaining performance characteristics related to driveability, fuel economy and reliability, they will meet with limited market interest at best.

5.0 CONCLUSIONS

From a public policy perspective, there are four conclusions which can be drawn from this market analysis.

First, there are significant deficiencies in the knowledge base on the availability and value of the aspen/poplar timber resource from which lignin would be obtained. To rectify these deficiencies, the following issues should be addressed:

- the cost and available supply of the resource; and,
- the relative values that can be generated from the resource through various uses such as manufacturing pulp, paper, and solid wood products, as well as from fuels and adhesives.

Second, much of the research into developing lignin as a substitute for phenol in adhesive resins and as a base substance from which fuel additives can be refined is based on using lignin that results as a co-product from a biomass liquefaction process. One of the processes that generates lignin is pulping. Traditionally, lignin derived from pulping has been used as an important and integral component in the energy cycle of pulp mills. Its potential diversion to other uses raises a number of questions about the impact on energy demand patterns in that industry. Little is known of these potential impacts and further analysis is required.

Third, the potential for lignin as a substitute for phenol in PF resins is of little benefit or interest if these resins become obsolete as a result of more stringent regulatory standards with regard to formaldehyde emissions. While this analysis has identified some of the key aspects of policy and regulation development on this issue, more detailed evaluation is required as a basis for guiding future research efforts on the potential for lignin in the development of new adhesives.

Fourth, the most important market characteristic with respect to evaluating the potential for alkyl aryl ethers, is the need for them to contribute to lower vehicle fuel and exhaust emissions when blended into motor fuels. Research focussed primarily or solely on achieving cost-competitiveness for alkyl aryl ethers relative to petrochemical-based ethers will likely result in a failure of the aryl ethers to gain any market position simply because they fail to address the primary needs of the market. The direction of the lignin research should therefore shift towards meeting the environmental imperatives of the fuels market, specifically emissions reduction and performance and driveability.

SECTION IV

CONCLUSIONS AND RECOMMENDATIONS

1.0 CONCLUSIONS

Batch ultrafiltration of alkaline extracts of steam-treated aspenwood water-insolubles yields polydisperse fractions. A substantial low molecular weight component may be present in the highest average molecular weight fractions. The characteristics of fractions obtained by ultrafiltration suggest that it may be inappropriate to fractionate this type of lignin into more than two or three fractions. The yields from constant volume and multiple batch ultrafiltrations of the alkaline extracts are similar, but not directly comparable with the yields from the fractionation of the ethyl acetate-extracted lignin and not comparable with the original ultrafiltration experiments. The results of constant volume and multiple batch ultrafiltrations suggests that there is a lignin or alkali concentration dependence to the ultrafiltration.

The preparation of the alkaline solution from the ethyl acetate-extracted lignin highlighted one of the problems with the lignin recovery method used. Method 2, which includes heating of the acidified lignin extract, leads to the production of alkali-insoluble material. The molecular weight distributions and properties of the lignins recovered after ultrafiltration are affected by the recovery process.

The acid precipitable lignins produced by anodic oxidation in basic aqueous media under go changes involving a decrease in phenyl groups and an increase of the carboxylic groups of the lignins and an opening of benzylic rings.

Characterization of the acetone-solubles recovered after electrolysis indicate drastic changes from the starting lignin. These changes are indicative of the formation of carbonyl carbons in esters or quinoidal structures, but the former interpretation is favored.

The yields of low molecular weight products produced by oxidation with increasing passage of charge indicate that the first formed products are undergoing further reaction.

Attempts to provide a parametric analysis of the electrolysis process were unsuccessful. However, the experiments indicated little production of volatile organic products and limited carbon dioxide production. Analysis of ethyl acetate solubles produced indicated the production of alkanedioic acids. Problems experienced with the analysis of the alkaline electrolysis solutions is an example of the difficulties encountered in analyzing lignin reaction products, and the need for analytical methods development.

Products of oxidation of steam-treated aspenwood lignin using peroxydisulfate, ($S_2O_8^{2-}$-Cu^{II}), in acetic acid are dependent on the available functional groups within the lignin, and can either lead to substantial depolymerization when the available hydroxyl functions are blocked and polymerization when they are available. Only low yields of monomeric products were obtained.

Metalloporphyrin oxidations on lignin were not investigated because of concerns with the observation of trace quantities of chlorinated products, the observation in two cases of oxidation in the absence of metal complex, and that when oxidation occurred only very low conversions were observed and products were dependent on starting material.

The low molecular weight lignin fractions from batch and constant volume ultrafiltration are more reactive for the formulation of lignin-phenolic adhesives than the corresponding higher molecular weight lignin-fractions. The unfractionated aspenwood lignin could be used to replace 10-20 % of a core PF waferboard adhesive and 30-40 % of a face PF waferboard adhesive.

Preparation of a powder, pre-cure resistant surface adhesive for waferboard demonstrated that steam-treated lignin could be used to replace 30% by solid weight of a phenol-formaldehyde in the formulation. The lignin-PF resin had a curing speed, similar to a commercial surface phenolic resin.

The sub-contract with Concordia University demonstrated that the steam-treated lignins could be successfully utilized in polyblend formulations with an epoxy (EP) adhesive (Ciba Geigy AY 103-HY 956). When compared with the EP control, the adhesive strength in shear of the EP-20% unfractionated lignin and EP-20% <10K lignin fraction disclosed superior performance, i.e., 15% and 30% higher respectively. The adhesive shear strength of the EP-<10K lignin fraction polyblends at a lignin content superior than 10%, after accelerated weathering is still higher than the EP control. In the same polyblends kraft lignins has little effect on shear strength. In the polyurethane (Desmodur E14-Desmophen 1920D)-lignin sealant systems, the effect of lignin upon the mechanical properties is less obvious than in the EP-L blends.

The cost estimation for the fractionation and recovery of lignin found the cost of fractionation of lignin using ultrafiltration followed by acid precipitation is estimated to be 17.5 cents/kg. This is 62% higher than the cost of lignin recovered by acid precipitation alone, which is estimated at 12 cents/kg.

The economic analysis of lignin use in wood products adhesives and as fuel octane enhancers led to the following four conclusions with respect to a public policy perspective.

There are significant deficiencies in the knowledge base on the availability and value of the aspen/poplar timber resource from which lignin would be obtained. To rectify these deficiencies, the following issues should be addressed: the cost and available supply of the resource; and, the relative values that can be generated from the resource through various uses such as manufacturing pulp, paper, and solid wood products, as well as from fuels and adhesives.

Much of the research into developing lignin as a substitute for phenol in adhesive resins and as a base substance from which fuel additives can be refined is based on using lignin that results as a co-product from a biomass liquefaction process. One of the processes that generates lignin is pulping. Traditionally, lignin derived from pulping has been used as an important and integral component in the energy cycle of pulp mills. Its potential diversion to other uses raises a number of questions about the impact on energy demand patterns in that industry. Little is known of these potential impacts and further analysis is required.

The potential for lignin as a substitute for phenol in PF resins is of little benefit or interest if these resins become obsolete as a result of more stringent regulatory standards with regard to formaldehyde emissions. While this analysis has identified some of the key aspects of policy and regulation development on this issue, more detailed evaluation is required as a basis for guiding future research efforts on the potential for lignin in the development of new adhesives.

The most important market characteristic with respect to evaluating the potential for alkyl aryl ethers, is the need for them to contribute to lower vehicle fuel and exhaust emissions when blended into motor fuels. Research focussed primarily or solely on achieving cost-competitiveness for alkyl aryl ethers relative to petrochemical-based ethers will likely result in a failure of the aryl ethers to gain any market position simply because they fail to address the primary needs of the market. The direction of the lignin research should therefore shift towards meeting the environmental imperatives of the fuels market, specifically emissions reduction and performance and driveability.

2.0 RECOMMENDATIONS

The significant deficiences in the knowledge base on the availability and value of the aspen/poplar timber resource from which lignin would be obtained must be addressed. The cost and available supply of the resource and the relative values that can be generated from the resource through alternative uses must be determined.

If the above analysis determines that continued research on this feedstock is worthwhile and warranted, then the following research on the production of low molecular weight chemicals by oxidation of lignin should be considered.

Electrochemical oxidation should be investigated using flow cells, using as feedstock acid precipitated lignin and the lignin containing alkaline extracts of steam-treated aspenwood. Peroxydisulfate, ($S_2O_8^{2-}$-Cu^{II}), oxidation of steam-treated aspenwood lignin and the acetylated and methylated derivatives should be examined under alkaline conditions. Water-soluble hemins, for example, meso-tetra(2,6-dichloro-3-sulfonatophenyl)porphyrin iron chloride, shown to catalyze many oxidation cycles of model lignin compounds merit attention and should be evaluated on available types of lignin in both aqueous and organic systems.

If any of the above demonstrate potential to produce increased yields of precursors for aryl methyl ethers then future research must take into account that the most important market characteristic with respect to evaluating the potential for alkyl aryl ethers, is the need for them to contribute to lower vehicle fuel and exhaust emissions when blended into motor fuels. The direction of the lignin research should therefore then shift towards meeting the environmental imperatives of the fuels market, specifically emissions reduction and performance and driveability. This latter directive is equally applicable to research directed at aryl methyl ethers regardless of the feedstock or conversion route.

More detailed evaluation of the policy and regulatory environment with respect to formaldehyde emissions is required as a basis for guiding future research efforts on the potential for lignin in the development of new adhesives. If this evaluation indicates that further development of lignin-PF adhesives is worthy of merit then the adhesives results for the powder, pre-cure resistant surface adhesive for waferboard demonstrated that steam-treated lignin could be demonstrated at pilot plant scale by the preparation of the powder adhesive on a sufficient scale to allow the manufacture of full size panels.

Epoxy-lignin polyblends demonstrated to be technically feasible, an economic assessment of their production is warranted to determine if it is economically viable.

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4.0 APPENDICES

APPENDIX 4.1

METHODS FOR FUSION DIAMETER TEST AND HOT PLATE CURE TEST

FUSION DIAMETER TEST

PURPOSE:

To determine the fluidity of a fusible heat reactive resin when heated on a hot plate at a specified temperature (150°C) and pressure (68 psi).

APPARATUS:

1. Hot plate, thermoelectric, preheated to 150 ± 1°C.
2. Analytical balance, ± 0.05 g accuracy.
3. Parr pellet press, 12.7 mm diameter pellet.
4. Stop watch.
5. Glass plate, 1/16" x 4" x 3" dimensions.
6. Weight cylinder, aluminum or steel, 6 kg.
7. Ruler.
8. Aluminum foil.

PROCEDURE:

1. Weigh upon a piece of paper 0.5 g of resin.
2. Using the par pellet press, make a pellet from the resin of diameter 12.7 mm and height 6.0 mm.
3. Transfer the pellet onto preheated hot plate, 150 ± 1°C, lined with aluminum foil. Immediately place glass plate followed by the weight cylinder on top of the pellet and start the stop watch.
4. After three min, remove the weight and measure the diameter of the melted pellet at 4 places.
5. Determine the average diameter and report as fusion diameter of the resin.

HOT PLATE CURE TEST

SCOPE:

This method is applicable to powdered phenolic resins. Lumps in resins are crushed before testing.

EQUIPMENT AND MATERIALS:

1. Cure plate, which can be controlled accurately at the required temperature 150°C.
2. A spatula with a stainless steel blade approximately 5" long by 15/16" wide.
3. Stopwatch.
4. Analytical balance capable of weighing 1.0 ± 0.05 g.

PROCEDURE:

1. Heat the cure plate to 150°C and maintain at 150 ± 2°C.
2. Apply a small quantity of slack wax or other molten wax to the cure plate.
3. Weigh 1.0 ± 0.05 g of sample onto a piece of paper.
4. Press the spatula blade against the cure plate surface for 10 to 15 sec so that the blade is heated.
5. Transfer the weighed sample to the centre of a 2" square area on cure plate surface and simultaneously start the stopwatch.
6. Apply pressure to the samplewith the hot spatula.
7. When the sample has melted, spread the molten sampleover the 2" square, using a slow sidewise smoothing motion of the spatula, with the leading edge slightly elevated. The spatula should be held at such an angle that approx. 1 1/4" of it's end is in contact with the cure plate. (Figure 1)
8. Keep the sample within the 2" square.
9. Stroke at a rate of one per second in a manner as shown in Figure 2. In stroking pull the blade forward and then lift it clear of the cure plate. Three strokes are required to cover the 2" square. Raise the spatula to a uniform height of 3/4" to 1" on each return stroke. repeat the six strokes as indicated in Figure 2, alternating between the sets with a continuous sidewise smoothing stroke.
10. Discontinue the sidewise smoothing stroke when strings begin to form. (the resin is no longer mobile).
11. Continue the six strokes until the resin no longer forms strings. The resin at this stage will be, non-tacky and will tend to snap back to the cure plate. A this stage stop the timer and record time as "cure time" or "gel time".
12. Scrape the resin immediately from the cure plate.

COMMENTS:

1. This test requires a high degree of manipulative skill. The success of the test, as a routine quality control test, lies largely in the skill of the operator and the control of the cure plate temperature.
2. Care should be taken to avoid scratching the cure plate surface when scraping the cured resin from the plate.

Figure 1

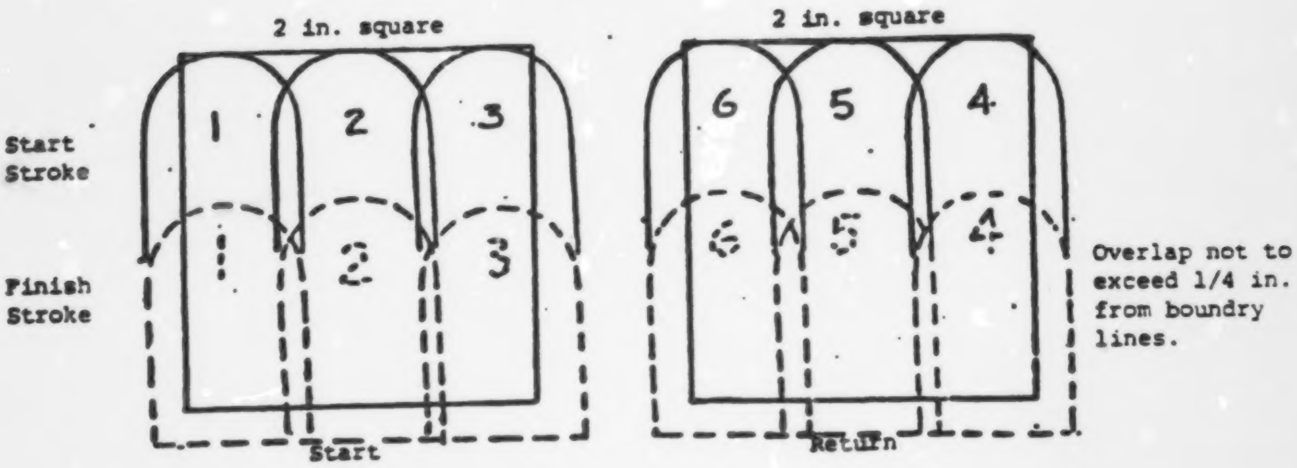
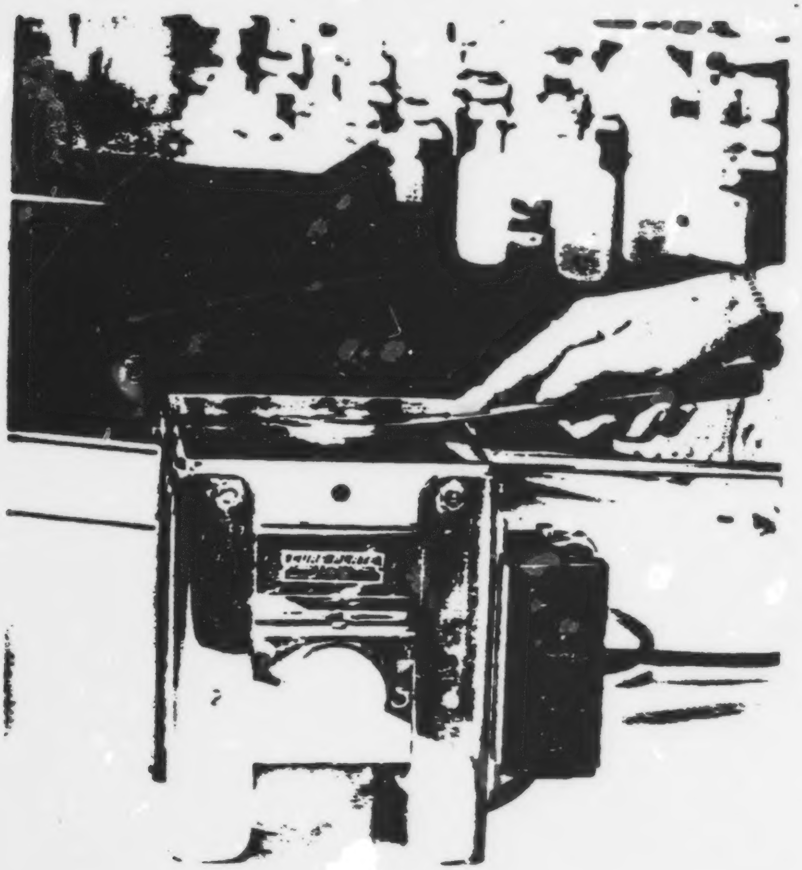

2 in. square
2 in. square
Start
Stroke
Finish
Stroke
1
2
3
6
5
4
Overlap not to
exceed 1/4 in.
from boundry
lines.
Start
Return

FIGURE 2



CURE PLATE

SAMPLE EVALUATION:

Resin type	Cure time (s)
Resin I	21, 22, 21
Resin II	39, 40, 40
Resin III	22, 18, 20

APPENDIX 4.2

DATA OF APPLIED POTENTIAL VERSUS CELL CURRENT DETERMINED IN ELECTROLYSIS EXPERIMENTS

LEAD DIOXIDE ANODE
APPLIED POTENTIAL (V vs SCE) VS CELL CURRENT (mA)

1M NaOH 25 deg-C

appl V	mA	mA/cm2	log mA/cm2
0.4	0	0	--
0.5	1	0.147928	-0.82994
0.6	15	2.218934	0.346144
0.65			
0.7	53	7.840236	0.894329
0.75	74	10.94674	1.039285
0.8	115	17.01183	1.230751
0.9	222	32.84023	1.516406

1M NaOh 25 deg-C 0.1g lignin

appl V	mA	mA/cm2	log mA/cm2
0.4	2	0.295857	-0.52891
0.5	4	0.591715	-0.22788
0.6	18	2.662721	0.425325
0.651	39	5.769230	0.761117
0.7	65	9.615384	0.982966
0.75	79	11.68639	1.067680
0.8	129	19.08284	1.280643
0.9	226	33.43195	1.524161

1M NaOh 25 deg-C 1.0g lignin

appl V	mA	mA/cm2	log mA/cm2
0.4	5	0.739644	-0.13097
0.501	9	1.331360	0.124295
0.601	25	3.698224	0.567993
0.651	42	6.213017	0.793302
0.7	68	10.05917	1.002562
0.751	102	15.08875	1.178653
0.8	142	21.00591	1.322341
0.9	246	36.39053	1.560988

3M NaOH 25 deg-C

appl V	mA	mA/cm2	log mA/cm2
0.4	1	0.147928	-0.82994
0.499	4	0.591715	-0.22788
0.551	11	1.627218	0.211445
0.6	24	3.550295	0.550264
0.65	39	5.769230	0.761117
0.701	73	10.79881	1.033376
0.75	110	16.27218	1.211445
0.8	165	24.40826	1.387537
0.9	313	46.30177	1.665597

3M NaOh 25 deg-C 0.1g lignin

appl V	mA	mA/cm2	log mA/cm2
0.301	0	0	--
0.401	3	0.443786	-0.35282
0.5	5	0.739644	-0.13097
0.55	14	2.071005	0.316181
0.601	32	4.733727	0.675203
0.65	53	7.840236	0.894329
0.7	88	13.01775	1.114535
0.75	129	19.08284	1.280643
0.8	179	26.47928	1.422906
0.9	316	46.74556	1.669748

3M NaOh 25 deg-C 1.0g lignin

appl V	mA	mA/cm2	log mA/cm2
0.2	2	0.295857	-0.52891
0.3	4	0.591715	-0.22786
0.4	5	0.739644	-0.13097
0.5	12	1.775147	0.249234
0.55	20	2.958579	0.471083
0.6	33	4.881656	0.688567
0.65	51	7.544378	0.877623
0.7	78	11.53846	1.062147
0.75	113	16.71597	1.223131
0.8	165	24.40828	1.387537
0.9	295	43.63905	1.639875

1M NaOh 70 deg-C

appl V	mA	mA/cm2	log mA/cm2
0.4	2	0.295857	-0.52891
0.501	14	2.071005	0.316181
0.551	44	6.508875	0.813505
0.601	88	13.01775	1.114535
0.649	136	20.11834	1.303592
0.701	199	29.43786	1.468906
0.75	267	39.49704	1.596564
0.8	345	51.03550	1.707872
0.9	520	76.92307	1.886056

1M NaOh 70 deg-C 0.1g lignin

appl V	mA	mA/cm2	log mA/cm2
0.301	6	0.887573	-0.05179
0.401	9	1.331360	0.124295
0.501	36	5.325443	0.726355
0.55	93	13.75739	1.138536
0.6	162	23.96449	1.379568
0.65	234	34.61538	1.539269
0.7	306	45.26627	1.655774
0.75	381	56.36094	1.750978
0.8	454	67.15976	1.827109
0.9	626	92.60355	1.966627

1M NaOh 70 deg-C 1.0g lignin

appl V	mA	mA/cm2	log mA/cm2
0.2	4	0.591715	-0.22788
0.3	10	1.479289	0.170053
0.4	13	1.923076	0.283996
0.5	44	6.508875	0.813505
0.55	115	17.01183	1.230751
0.6	192	28.40236	1.453354
0.65	276	40.82840	1.610962
0.7	358	52.95857	1.723936
0.75	443	65.53254	1.816457
0.8	535	79.14201	1.898407
0.9	714	105.6213	2.023751

3M NaOh 70 deg-C

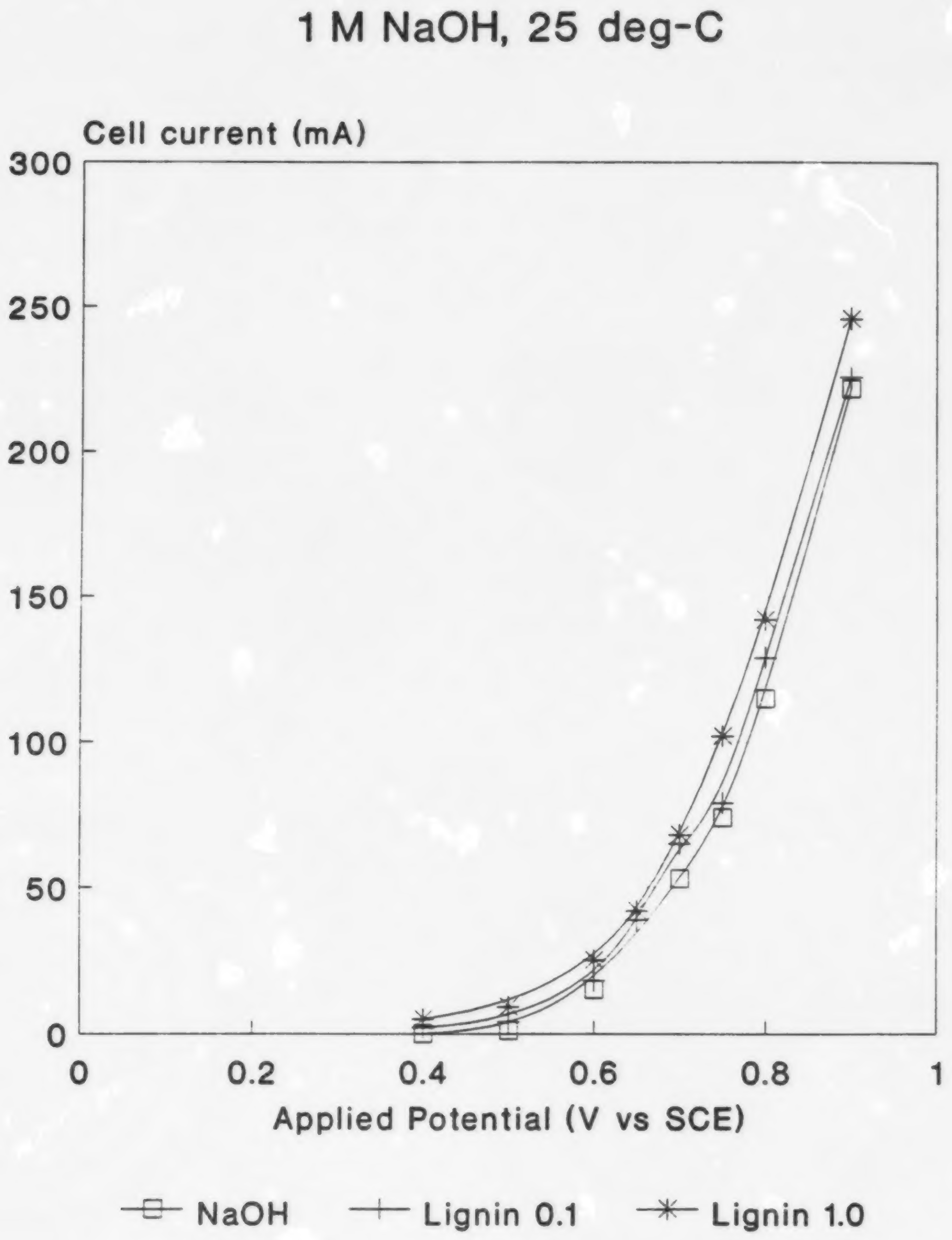
appl V	mA	mA/cm2	log mA/cm2
0.299	3	0.443786	-0.35282
0.4	9	1.331360	0.124295
0.45	13	1.923076	0.283996
0.5	34	5.029585	0.701532
0.551	63	9.319526	0.969393
0.601	98	14.49704	1.161279
0.65	135	19.97041	1.300387
0.7	199	29.43786	1.468906
0.751	277	40.97633	1.612533
0.8	359	53.10650	1.725147
0.9	538	79.58579	1.900835

3M NaOh 70 deg-C 0.1g lignin

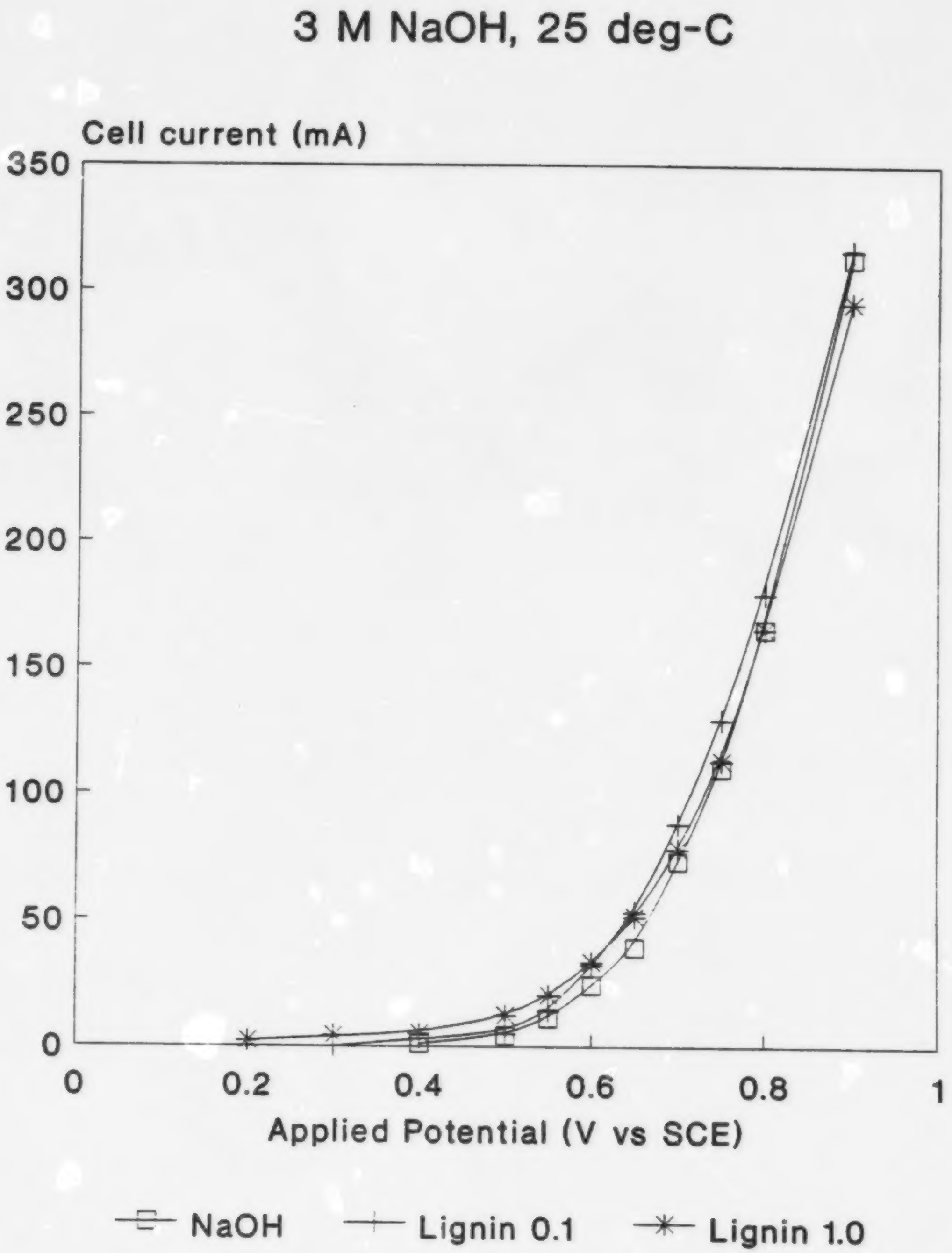
appl V	mA	mA/cm2	log mA/cm2
0.3	8	1.183431	0.073143
0.401	13	1.923076	0.283996
0.45	26	3.846153	0.585026
0.5	79	11.68639	1.067680
0.55	141	20.85798	1.319272
0.6	206	30.47337	1.483920
0.651	268	39.64497	1.598188
0.7	330	48.81656	1.688567
0.751	396	58.57988	1.767748
0.8	467	69.08284	1.839370
0.9	628	92.89940	1.968012

3M NaOh 70 deg-C 1.0g lignin

appl V	mA	mA/cm2	log mA/cm2
0.3	12	1.775147	0.249234
0.4	22	3.254437	0.512475
0.451	40	5.917159	0.772113
0.5	91	13.46153	1.129094
0.55	178	26.33136	1.420473
0.601	265	39.20118	1.593299
0.65	357	52.81065	1.722721
0.7	446	65.97633	1.819388
0.75	532	78.69822	1.895964
0.8	614	90.82840	1.958221



LEAD DIOXIDE



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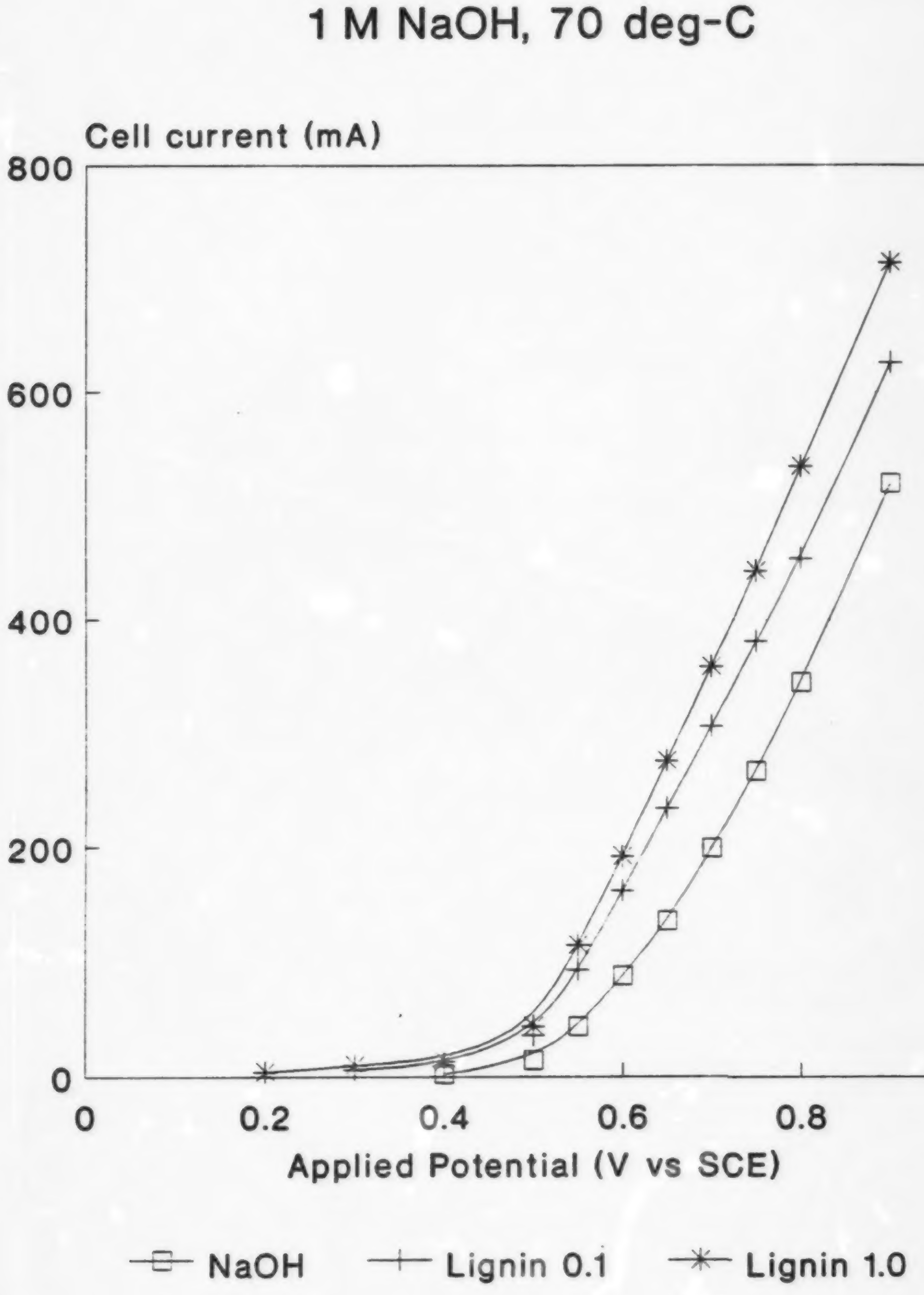

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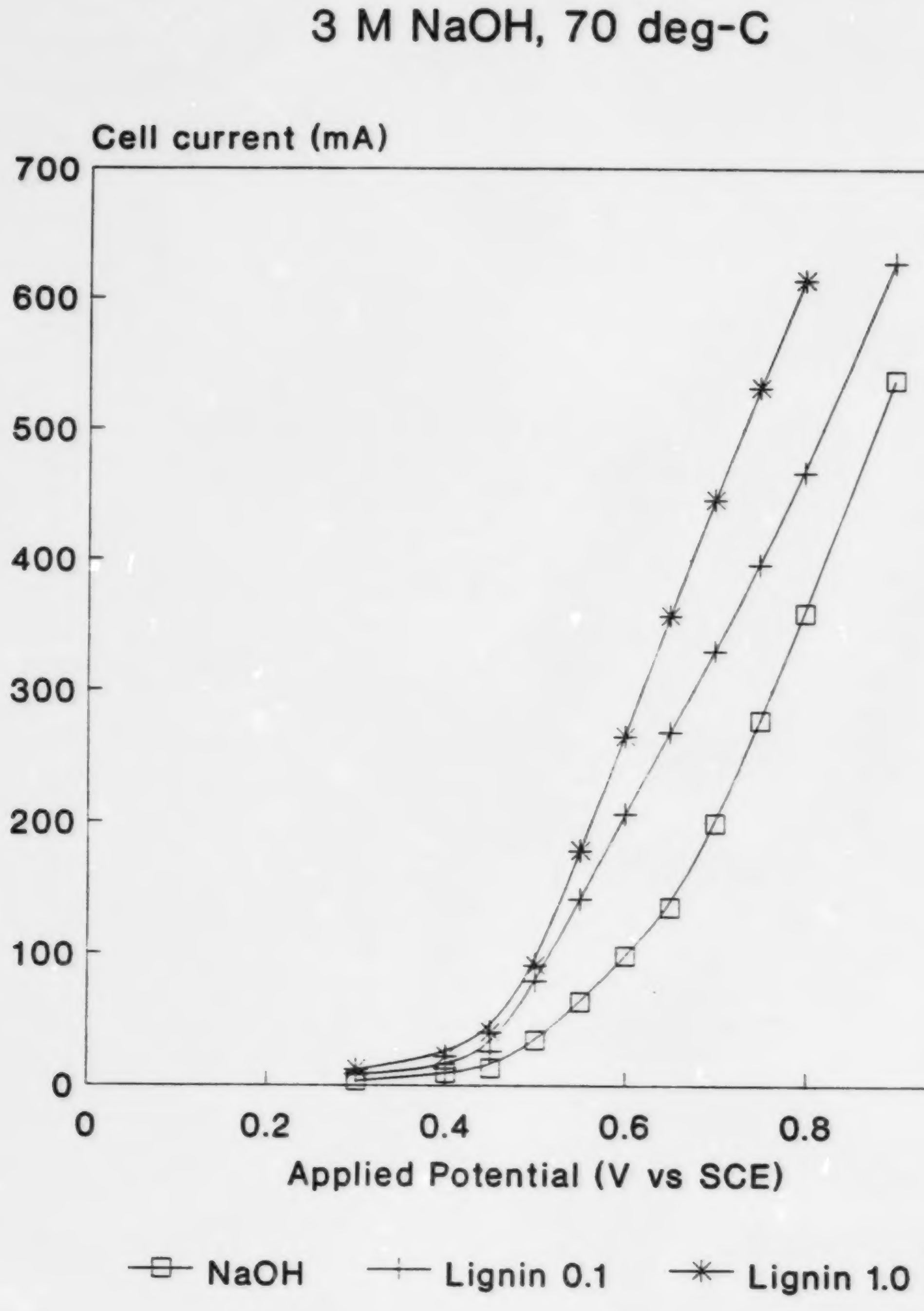


LEAD DIOXIDE

FOAM NICKEL ANODE 30 pore 2%
APPLIED POTENTIAL (V vs SCE) VS CELL CURRENT (mA)

1M NaOh 25 deg-C

appl V	mA	mA/cm2	log mA/cm2
0.1	1	0.16	-0.79588
0.2	1	0.16	-0.79588
0.3	1	0.16	-0.79588
0.4	2	0.32	-0.49485
0.5	10	1.6	0.204119
0.6	103	16.48	1.216957
0.7	296	47.36	1.675411
0.8	558	89.28	1.950754

1M NaOH 25 deg-C 0.1g lignin

appl V	mA	mA/cm2	log mA/cm2
0.1	0	0	--
0.2	1	0.16	-0.79588
0.3	3	0.48	-0.31875
0.4	8	1.28	0.107209
0.5	18	2.88	0.459392
0.6	132	21.12	1.324693
0.7	361	57.76	1.761627
0.8	592	94.72	1.976441

1M NaOh 25 deg-C 1.0g lignin

appl V	mA	mA/cm2	log mA/cm2
0.1	3	0.48	-0.31875
0.2	6	0.96	-0.01772
0.3	12	1.92	0.283301
0.4	28	4.48	0.651278
0.5	69	11.04	1.042969
0.6	295	47.2	1.673941
0.7	633	101.28	2.005523
0.8			

3M NaOh 25 deg-C

appl V	mA	mA/cm2	log mA/cm2
0.1	0	0	--
0.2	0	0	--
0.3	2	0.32	-0.49485
0.4	3	0.48	-0.31875
0.5	71	11.36	1.055378
0.6	328	52.48	1.719993
0.7	653	104.48	2.019033

3M NaOh 25 deg-C 0.1g lignin

appl V	mA	mA/cm2	log mA/cm2
0.1	0	0	--
0.2	1	0.16	-0.79588
0.3	5	0.8	-0.09691
0.4	10	1.6	0.204119
0.5	84	13.44	1.128399
0.6	367	58.72	1.768786
0.7	695	111.2	2.046104

3M NaOh 25 deg-C 1.0g lignin

appl V	mA	mA/cm2	log mA/cm2
0.1	5	0.8	-0.09691
0.2	8	1.28	0.107209
0.3	15	2.4	0.380211
0.4	35	5.6	0.748188
0.5	136	21.76	1.337658
0.6	461	73.76	1.867820
0.7	799	127.84	2.106666

1M NaOh 70 deg-C

appl V	mA	mA/cm2	log mA/cm2
0.1	1	0.16	-0.79588
0.2	1	0.16	-0.79588
0.3	3	0.48	-0.31875
0.4	18	2.88	0.459392
0.5	230	36.8	1.565847
0.6	596	95.36	1.979366
0.65	783	125.28	2.097881

1M NaOh 70 deg-C 0.1g lignin

appl V	mA	mA/cm2	log mA/cm2
0.1	5	0.8	-0.09691
0.2	9	1.44	0.158362
0.3	20	3.2	0.505149
0.4	71	11.36	1.055378
0.5	325	52	1.716003
0.6	737	117.92	2.071587
0.65	949	151.84	2.181386

1M NaOh 70 deg-C 1.0g lignin

appl V	mA	mA/cm2	log mA/cm2
0.1	18	2.88	0.459392
0.2	23	3.68	0.565847
0.3	44	7.04	0.847572
0.4	182	29.12	1.464191
0.5	472	75.52	1.878061
0.6	878	140.48	2.147614
0.65			

3M NaOh 70 deg-C

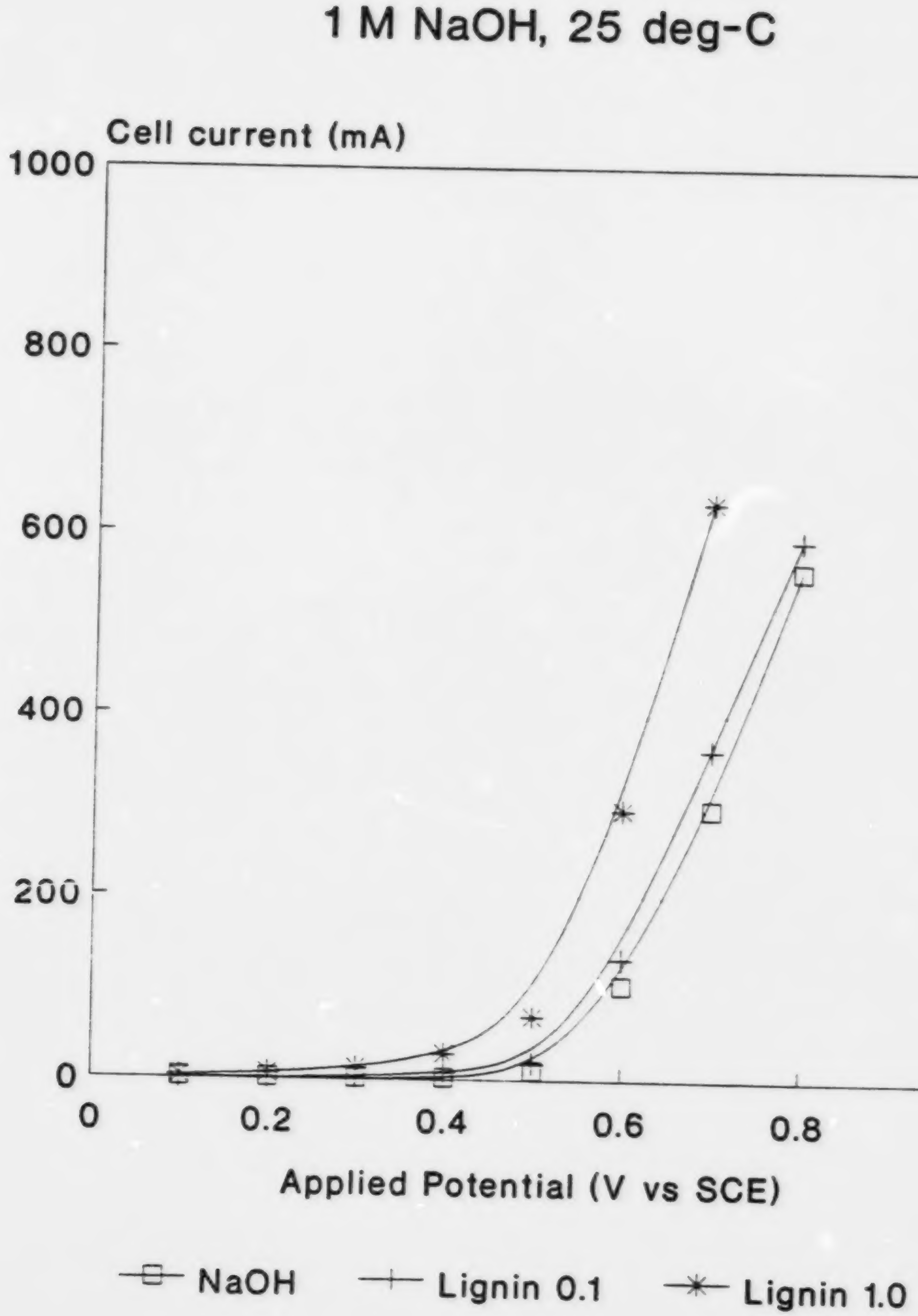
appl V	mA	mA/cm2	log mA/cm2
0.1	1	0.16	-0.79588
0.2	3	0.48	-0.31875
0.3	10	1.6	0.204119
0.4	105	16.8	1.225309
0.5	447	71.52	1.854427
0.55	689	110.24	2.042339
0.6	945	151.2	2.179551

3M NaOh 70 deg-C 0.1g lignin

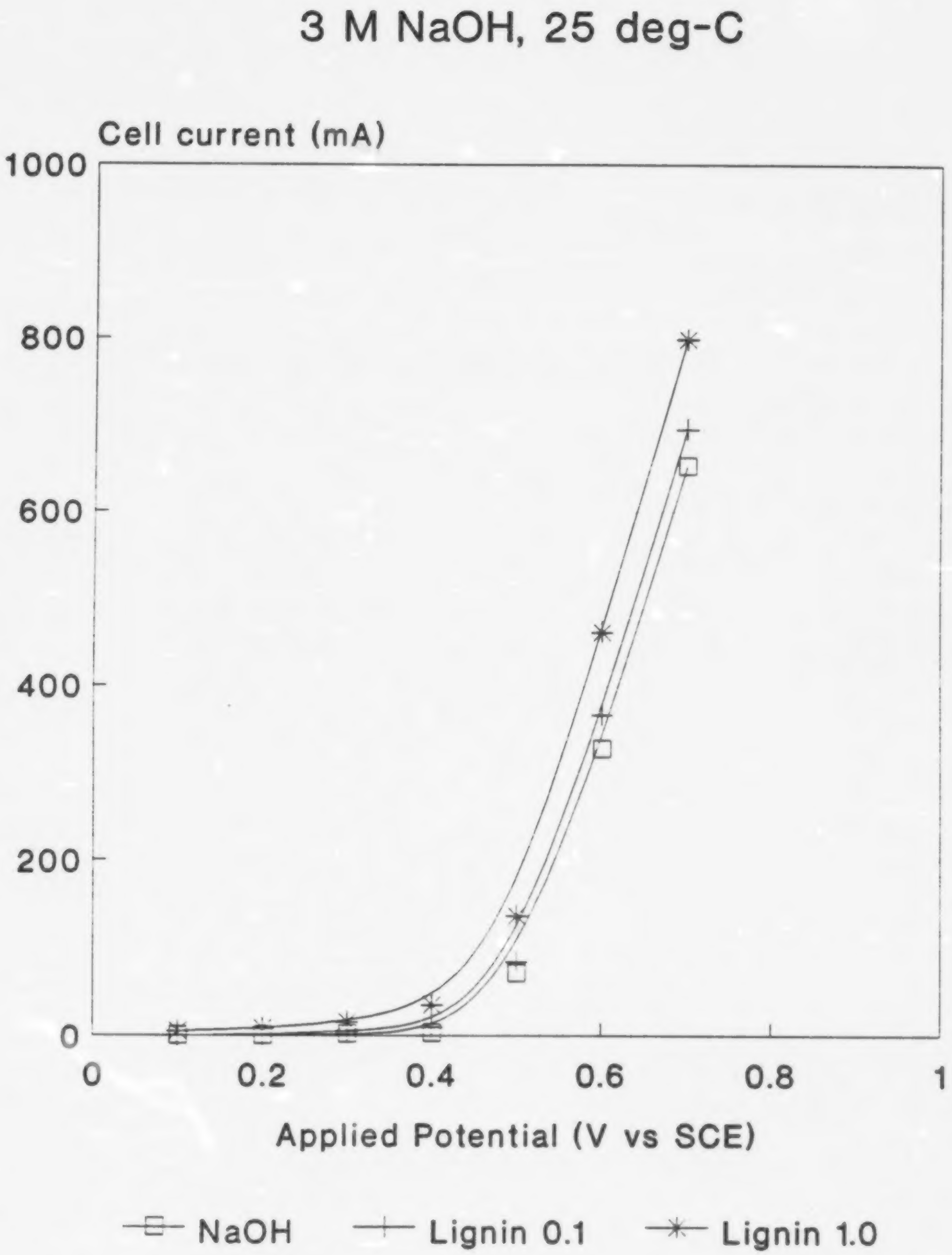
appl V	mA	mA/cm2	log mA/cm2
0.1	12	1.92	0.283301
0.2	22	3.52	0.546542
0.3	65	10.4	1.017033
0.4	200	32	1.505149
0.5	560	89.6	1.952308
0.55	761	121.76	2.085504
0.6			

3M NaOh 70 deg-C 1.0g lignin

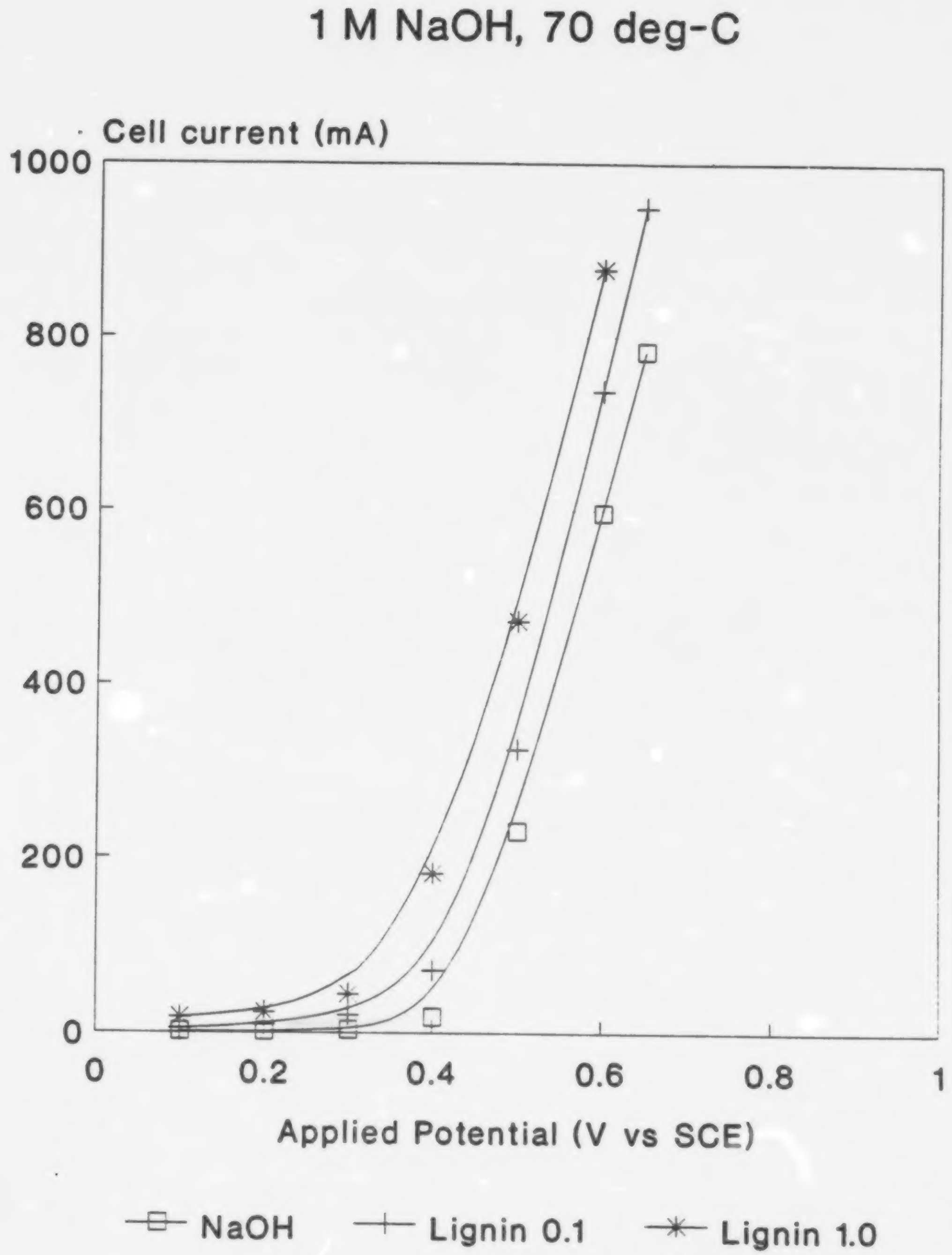
appl V	mA	mA/cm2	log mA/cm2
0.1	20	3.2	0.505149
0.2	27	4.32	0.635483
0.3	94	15.04	1.177247
0.4	271	43.36	1.637089
0.5	605	96.8	1.985875
0.55	826	132.16	2.121100
0.6			


1 M NaOH, 25 deg-C
Cell current (mA)
1000
800
600
400
200
0
0
0.2
0.4
0.6
0.8
1
Applied Potential (V vs SCE)
NaOH
Lignin 0.1
Lignin 1.0

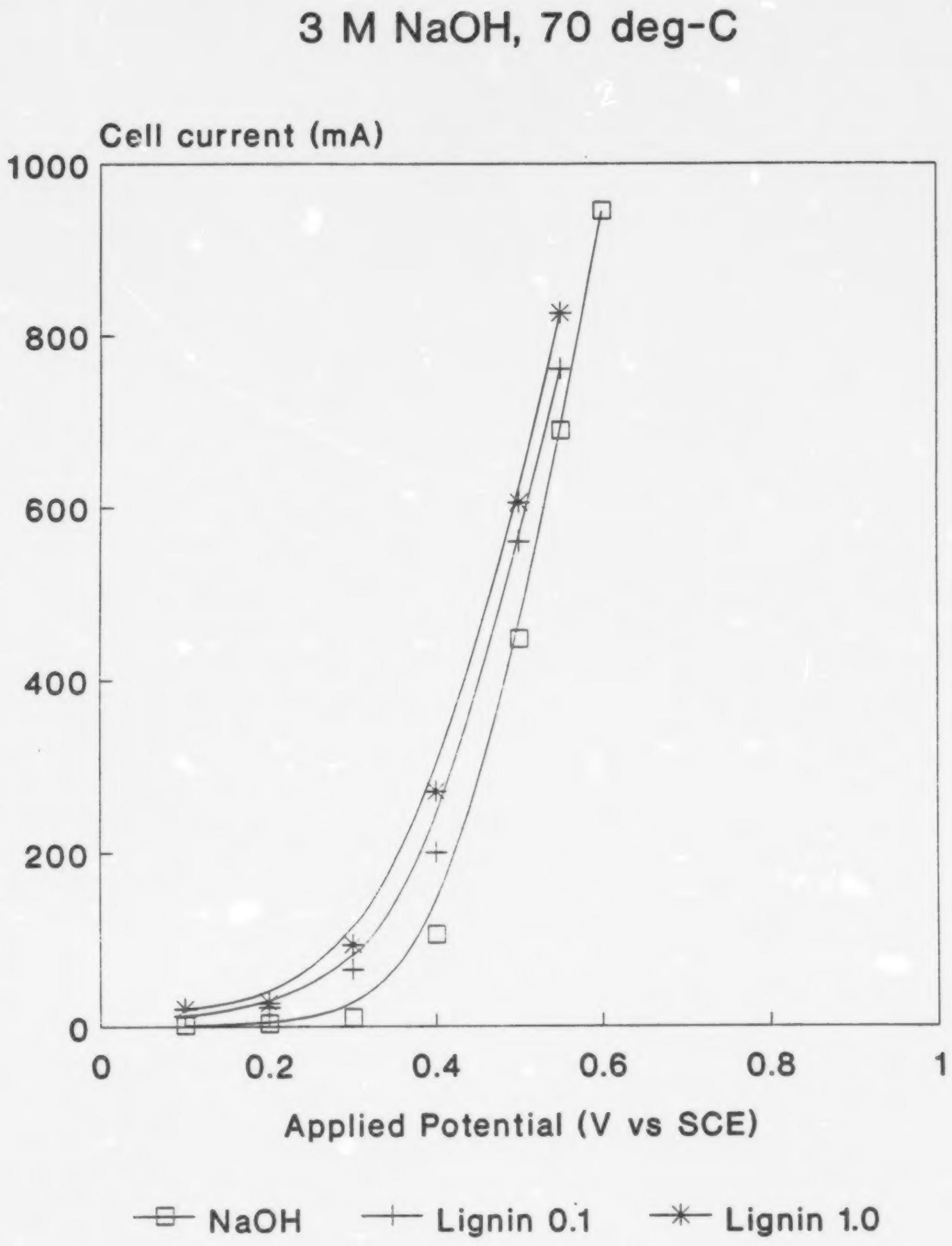
FOAMNICKEL


3 M NaOH, 25 deg-C
Cell current (mA)
1000
800
600
400
200
0
0
0.2
0.4
0.6
0.8
1
Applied Potential (V vs SCE)
NaOH
Lignin 0.1
Lignin 1.0

FOAMNICKEL


1 M NaOH, 70 deg-C
Cell current (mA)
1000
800
600
400
200
0
0
0.2
0.4
0.6
0.8
1
Applied Potential (V vs SCE)
NaOH
Lignin 0.1
Lignin 1.0

FOAMNICKEL


3 M NaOH, 70 deg-C
Cell current (mA)
1000
800
600
400
200
0
0
0.2
0.4
0.6
0.8
1
Applied Potential (V vs SCE)
NaOH
Lignin 0.1
Lignin 1.0

FOAMNICKEL

PLATINUM ANODE
APPLIED POTENTIAL (V vs SCE) VS CELL CURRENT (mA)

1M NaOH 25 deg-C

appl V	mA	mA/cm2	log mA/cm2
0.1	0	0	--
0.2	0	0	--
0.3	0	0	--
0.4	0	0	--
0.5	0	0	--
0.6	2	0.32	-0.49485
0.7	12	1.92	0.283301
0.8	21	3.36	0.526339
0.9	34	5.44	0.735598
1	86	13.76	1.138618

1M NaOH 25 deg-C 0.1g lignin

appl V	mA	mA/cm2	log mA/cm2
0.1	0	0	--
0.2	0	0	--
0.3	1	0.16	-0.79588
0.4	1	0.16	-0.79588
0.5	1	0.16	-0.79588
0.6	4	0.64	-0.19382
0.7	8	1.28	0.107209
0.8	10	1.6	0.204119
0.9	20	3.2	0.505149
1	56	8.96	0.952308

1M NaOH 25 deg-C 1.0g iignin

appl V	mA	mA/cm2	log mA/cm2
0.1	1	0.16	-0.79588
0.2	1	0.16	-0.79588
0.3	1	0.16	-0.79588
0.4	1	0.16	-0.79588
0.5	2	0.32	-0.49485
0.6	6	0.96	-0.01772
0.7	13	2.08	0.318063
0.8	19	3.04	0.482873
0.9	24	3.84	0.584331
1	46	7.36	0.866877

3M NaOH 25 deg-C

appl V	mA	mA/cm2	log mA/cm2
0.1	0	0	--
0.2	0	0	--
0.3	0	0	--
0.4	0	0	--
0.5	0	0	--
0.6	1	0.16	-0.79588
0.7	4	0.64	-0.19382
0.8	9	1.44	0.158362
0.9	27	4.32	0.635483
1	125	20	1.301029

3M NaOH 25 deg-C 0.1g lignin

appl V	mA	mA/cm2	log mA/cm2
0.1	0	0	--
0.2	0	0	--
0.3	0	0	--
0.4	1	0.16	-0.79588
0.5	1	0.16	-0.79588
0.6	3	0.48	-0.31875
0.7	5	0.8	-0.09691
0.8	8	1.28	0.107209
0.9	18	2.88	0.459392
1	63	10.08	1.003460

3M NaOH 25 deg-C 1.0g lignin

appl V	mA	mA/cm2	log mA/cm2
0.1	0	0	--
0.2	1	0.16	-0.79588
0.3	1	0.16	-0.79588
0.4	1	0.16	-0.79588
0.5	2	0.32	-0.49485
0.6	4	0.64	-0.19382
0.7	6	0.96	-0.01772
0.8	11	1.76	0.245512
0.9	22	3.52	0.546542
1	55	8.8	0.944482

1M NaOH 70 deg-C

appl V	mA	mA/cm2	log mA/cm2
0.1	0	0	--
0.2	0	0	--
0.3	0	0	--
0.4	0	0	--
0.5	2	0.32	-0.49485
0.6	10	1.6	0.204119
0.7	25	4	0.602059
0.8	60	9.6	0.982271
0.9	142	22.72	1.356408

1M NaOH 70 deg-C 0.1g iignin

appl V	mA	mA/cm2	log mA/cm2
0.1	1	0.16	-0.79588
0.2	1	0.16	-0.79588
0.3	1	0.16	-0.79588
0.4	2	0.32	-0.49485
0.5	8	1.28	0.107209
0.6	16	2.56	0.408239
0.7	27	4.32	0.635483
0.8	67	10.72	1.030194
0.9	143	22.88	1.359456

1M NaOH 70 deg-C 1.0g iignin

appl V	mA	mA/cm2	log mA/cm2
0.1	2	0.32	-0.49485
0.2	2	0.32	-0.49485
0.3	2	0.32	-0.49485
0.4	3	0.48	-0.31875
0.5	13	2.08	0.318063
0.6	30	4.8	0.681241
0.7	56	8.96	0.952308
0.8	90	14.4	1.158362
0.9	106	16.96	1.229425

3M NaOH 70 deg-C

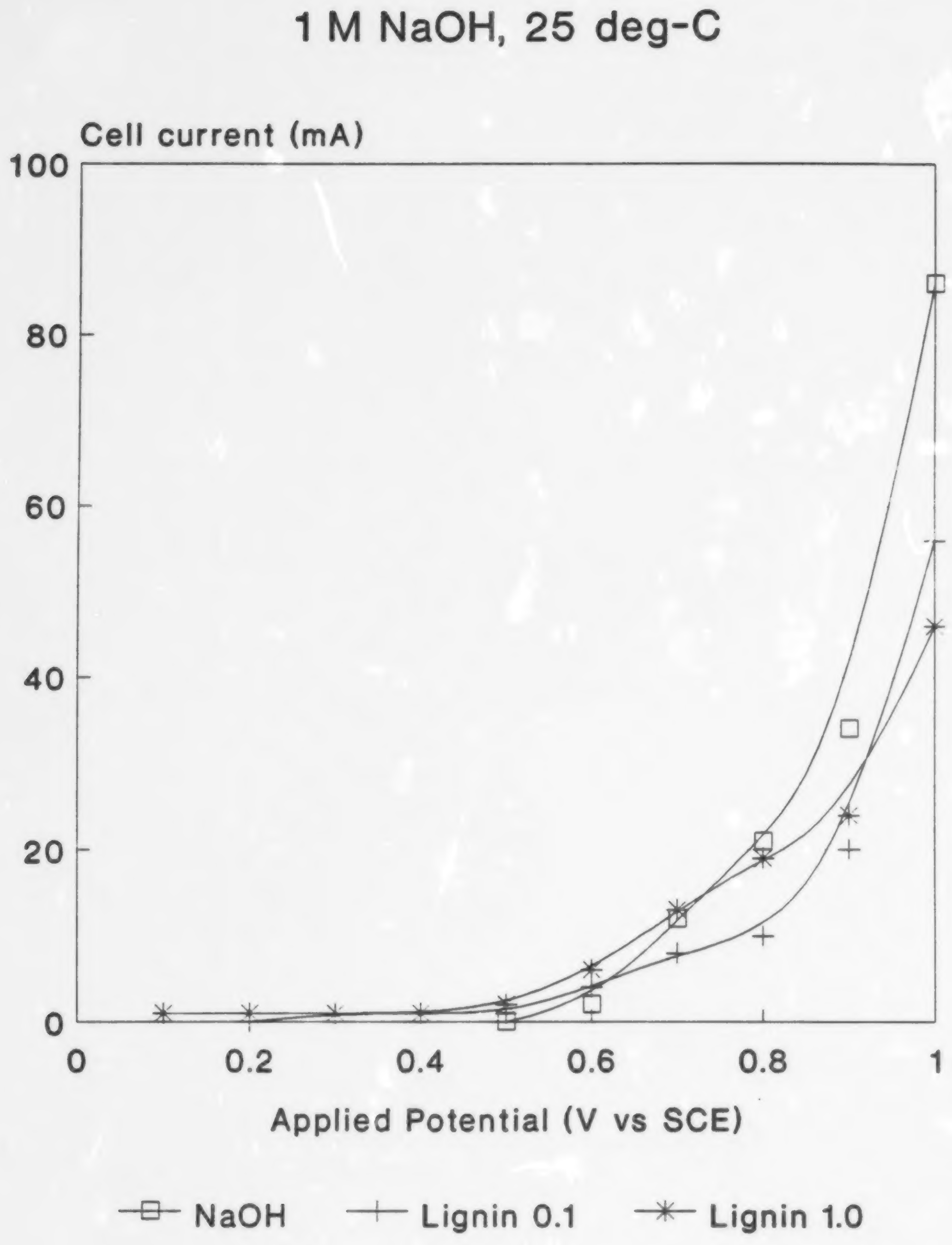
appl V	mA	mA/cm2	log mA/cm2
0.1	0	0	--
0.2	0	0	--
0.3	0	0	--
0.4	0	0	--
0.5	3	0.48	-0.31875
0.6	8	1.28	0.107209
0.7	29	4.64	0.666517
0.8	80	12.8	1.107209
0.9	259	41.44	1.617419

3M NaOH 70 deg-C 0.1g iignin

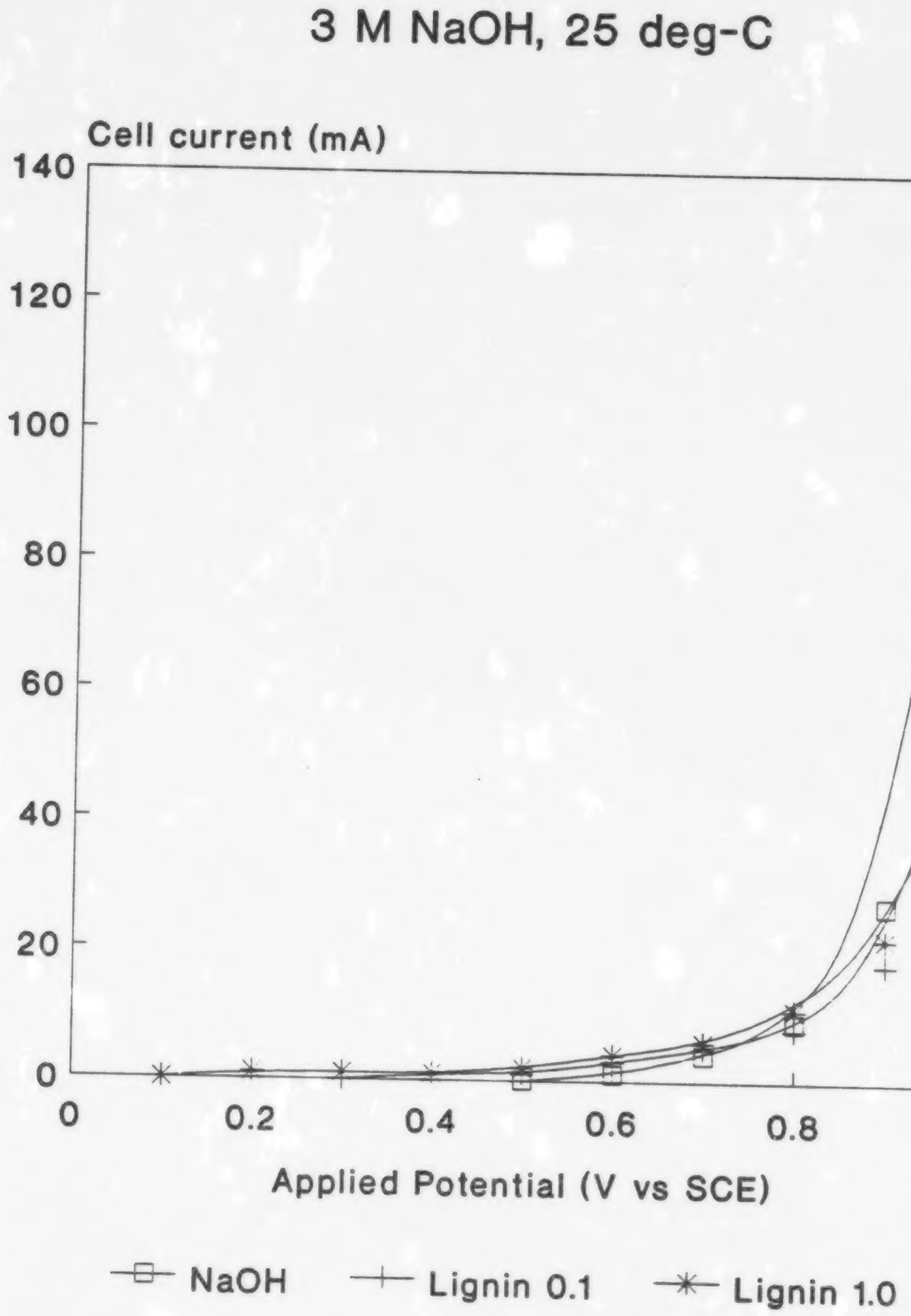
appl V	mA	mA/cm2	log mA/cm2
0.1	1	0.16	-0.79588
0.2	1	0.16	-0.79588
0.3	1	0.16	-0.79588
0.4	2	0.32	-0.49485
0.5	7	1.12	0.049218
0.6	12	1.92	0.283301
0.7	33	5.28	0.722633
0.8	74	11.84	1.073351
0.9	187	29.92	1.475961

3M NaOH 70 deg-C 1.0g lignin

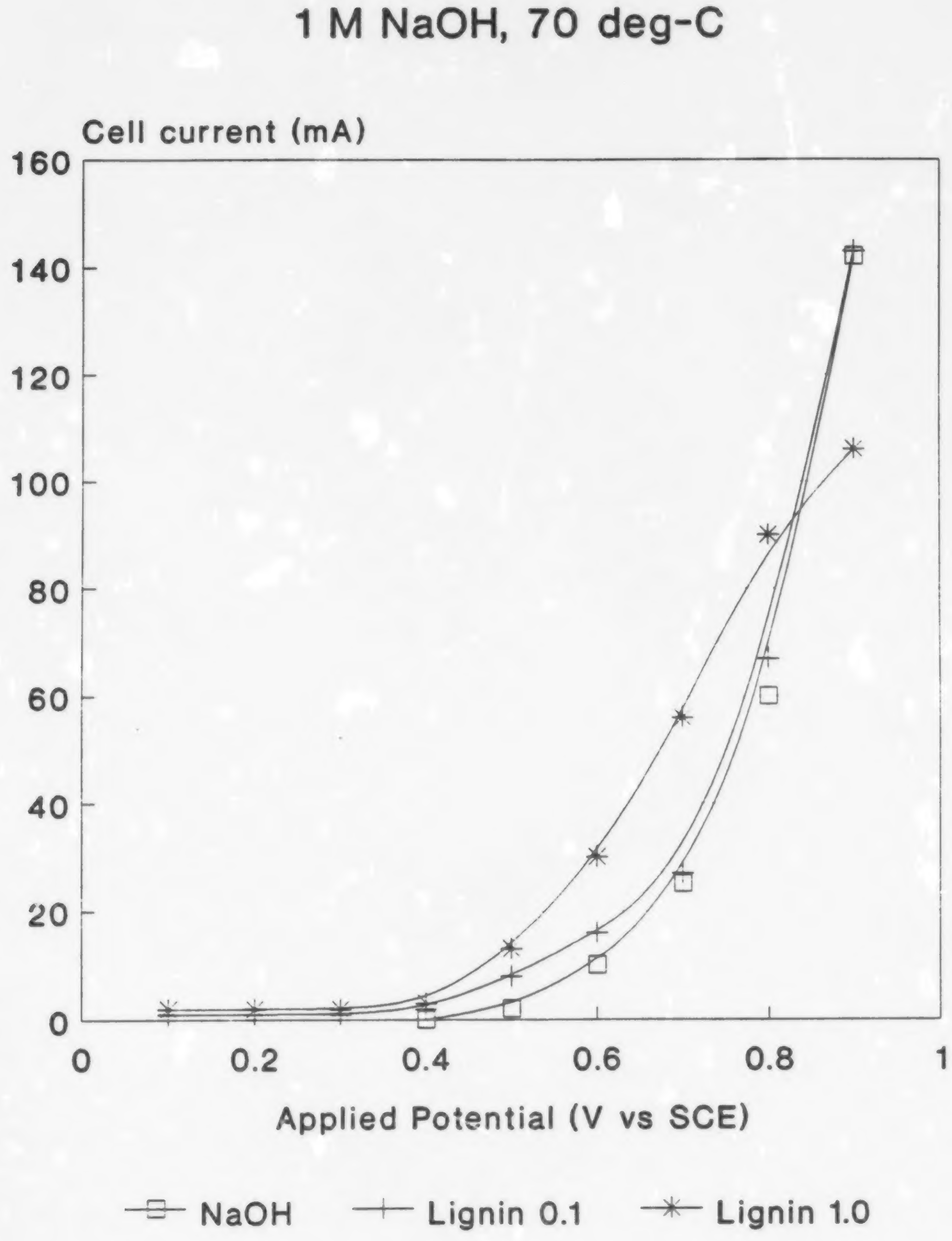
appl V	mA	mA/cm2	log mA/cm2
0.1	1	0.16	-0.79588
0.2	2	0.32	-0.49485
0.3	3	0.48	-0.31875
0.4	6	0.96	-0.01772
0.5	22	3.52	0.546542
0.6	44	7.04	0.847572
0.7	72	11.52	1.061452
0.8	102	16.32	1.212720
0.9	167	26.72	1.426836


1 M NaOH, 25 deg-C
Cell current (mA)
100
80
60
40
20
0
0
0.2
0.4
0.6
0.8
1
Applied Potential (V vs SCE)
NaOH
Lignin 0.1
Lignin 1.0

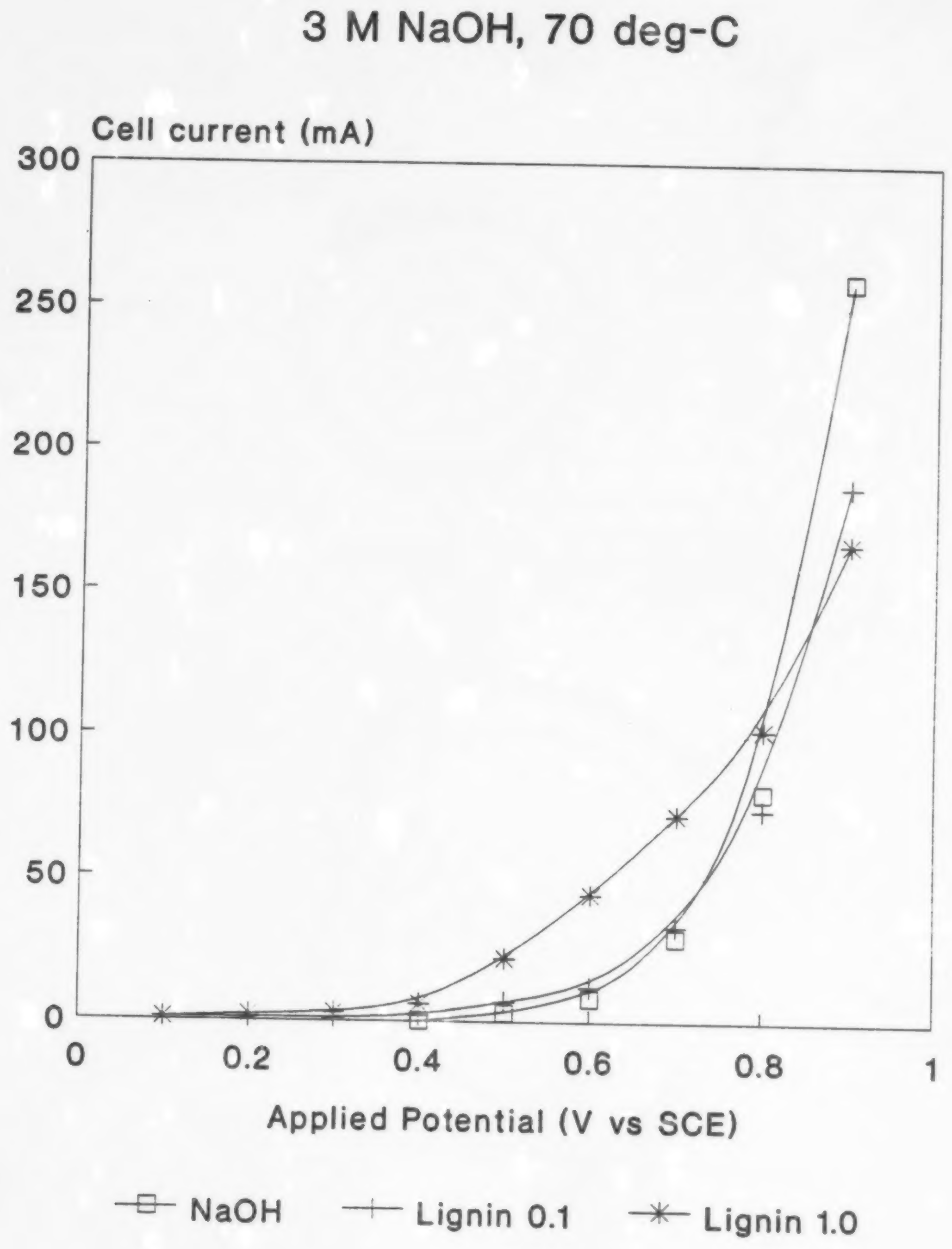
PLATINUM


3 M NaOH, 25 deg-C
Cell current (mA)
140
120
100
80
60
40
20
0
0
0.2
0.4
0.6
0.8
1
Applied Potential (V vs SCE)
NaOH
Lignin 0.1
Lignin 1.0

PLATINUM


1 M NaOH, 70 deg-C
Cell current (mA)
160
140
120
100
80
60
40
20
0
0
0.2
0.4
0.6
0.8
1
Applied Potential (V vs SCE)
NaOH
Lignin 0.1
Lignin 1.0

PLATINUM


3 M NaOH, 70 deg-C
Cell current (mA)
300
250
200
150
100
50
0
0
0.2
0.4
0.6
0.8
1
Applied Potential (V vs SCE)
NaOH
Lignin 0.1
Lignin 1.0

PLATINUM

SENSITIVITY ANALYSIS RESULTS

Table 1

Effect of Lignin Concentration in Caustic Extract

Lignin conc. (wt %)	Lignin price (cents/kg) ACID	UF
1	41.4	58.6
2	21.8	31.2
3	15.3	22.1
4	12.0	17.5
5	10.0	14.7

Table 2

Effect of Caustic Concentration

CNaOH (wt %)	Lignin price (cents/kg) ACID	UF
0.4	12.0	17.5
0.6	15.5	21.7
0.8	19.0	26.0
1.0	22.5	30.3

Table 3

Effect of Lignin Recovery Yield

Yield (%)	Lignin price (cents/kg) ACID	UF
70	13.6	19.8
75	12.7	18.6
80	12.0	17.5
85	11.3	16.5
90	10.8	15.7

Table 4

Effect of Ultrafiltration Flux

Flux ($L/m^2.h$)	Lignin price (cents/kg) UF
20	17.8
40	17.5
60	17.3
80	17.2

Table 5

Effect of Moisture Content of Filtered Lignin

Moisture Content (wt %)	Lignin price (cents/kg)	
	ACID	UF
40	11.8	17.3
50	12.0	17.5
60	12.2	17.7
70	12.4	17.9

APPENDIX 4.5

WORK PLAN AND REPORT FOR CONCORDIA SUB-CONTRACT ENTITLED "STEAM-EXPLODED LIGNIN UTILIZATION AS A NEW ADDITIVE FOR BUILDING MATERIALS"

Preliminary work plan for the subcontract between Dr. Feldman, Concordia University and Forintek Canada Corp., entitled "Steam-exploded lignin utilisation as a new additive for building materials"

Preliminary screening will be undertaken using steam-exploded lignin in a polyurethane (PU) sealant and an epoxy (EP) adhesive system, to provide a comparison with kraft lignins in PU and EP systems.

Lignin samples: Forintek will provide unfractionated lignin from steam-exploded aspenwood. The lignin will be recovered from water-washed, steam-exploded aspenwood by alkaline extraction and isolated by acid precipitation and heat treatment. This lignin will be used in both PU and EP systems.

Two fractions of this lignin obtained by ultrafiltration will be provided for use in EP tests.

Preparation of test samples

The lignin samples will be blended in the PU and EP systems at 5, 10, 15 and 20% substitute levels. The resulting blends will be tested with aluminum substrates. Appropriate controls will be prepared. Artificial weathering will be performed cycling -30°C to +30°C.

Tests

	Property	Method
1.	Curing characteristic, Glass Transition temperature (Tg) comparability between blend components	Differential scanning calorimetry
2.	"Bonding" information	UV spectroscopy
3.	Shear strength Cohesive and adhesive strength	Mechanical tests

If necessary, dynamic mechanical analysis will be undertaken, and performance properties will be tested in accordance with established procedures (ASTM, CSA).

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Steam - Exploded Lignin Utilization as a New Additive for Building Materials

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Project No. CBS- 141

Title: Steam - Exploded Lignin Utilization as a new Additive for Building Materials.

Author(s): D. Feldman, D. Banu, M. Lacasse, C. Luchian, J. Wang

Verificator: Dr. D. Feldman

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No. du projet CBS- 141

Titre: Steam - Exploded Lignin Utilization comme nouveau Additif poue les materiaux de construction.

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Verificateur: Dr. D. Feldman

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800 Montreal Rd, Ottawa
Ontario K1G 3K5

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Fazio

P. Fazio

Director

Directeur

FINAL REPORT

CONCERNING THE RESULTS OBTAINED FOR THE SUBCONTRACT

Steam exploded lignin utilization as a new additive for building materials

I INTRODUCTION

On september 26, 1989, the following 3 samples of steam exploded lignin (SEL were obtained from FORINTEK CANADA Corp.:

- unfractionated SEL (M_w = 6752, M_n = 985)
- 30-100 K fraction (M_w = 9447, M_n = 1128)
- < 10 K fraction (M_w = 3103, M_n = 594)

In principle, the study implies the preparation of polyblends of SEL with a polyurethane (PU) sealant and an epoxy (EP) adhesive and to compare their performances with those of the polyblends made with Kraft lignin (L) (Tomlinite, Domtar) which has the following characteristics:

- Molecular weight: M_w = 2785; M_n = 648
- Elemental analysis: C% = 65.06
  H% = 6.03
  S% = 1.59
- Functional groups: Total 0H%: 10.7
  Methoxyl%: 17.2
  Carbonyl%: 5.0
- Specific gravity: 1.28 g/cm^3

a) Lignin samples were blended in PU and EP systems at 5, 10, 15 and 20% substitute levels. The resulting blends were tested for mechanical properties with aluminum substrates. The mechanical tests were performed after the apparently complete cure of polyblends as well as after an artificial weathering in an environmental chamber at 4 cycles per day in the temperature range -28... + 33°C. The EP-L's polyblends were cycled for 180 days and the PU-L's polyblends for 93 days.

b) The effect of L's on the crosslinking kinetics of the EP was studied by differential scanning calorimetry (DSC). Compatibility of L's with PU and EP was determined too by DSC from the polyblends glass transition data.

c) The degree of bonding of different kinds of L to PU or EP was established by extraction and UV spectroscopy.

2. INSTRUMENTATION

(a) An Instron Universal Testing Machine model 1125 was used to asses the tensile properties of the blends. In the case of the PU-L's blends the elongation of the specimens was determined using a Sony CCD-F40 video camera in which the continuous recording of the test was made. The strain in the elastomer was evaluated by measuring the change in gauge length (25.4 mm) against a millimetric scale placed adjacent to the specimen. The maximum specimen elongation at the point of rupture, was recorded directly from a video screen. The specimens were tested at a rate of 50 mm/min until rupture occurred. The load at rupture was recorded and the elongation at rupture was evaluated using the video recording as described above.

(b) The same Instron testing machine was used for the determination of the EP-L's adhesive shear strength using tensile load. The specimens were tested at a rate of 15 mm/min.

(c) The Kinetic data as well as the glass transition temperatures were obtained with a DuPont 1090 Thermal Analyzer - 910 Differential Scanning Calorimeter. All the experiments were performed in nitrogen atmosphere. For the kinetic characterisation, tests were run at a heating rate of 10°C/min. from - 30 to 220°C and at a heating rate of 20°C/min. for the Tg determination. The Tg scans were performed from -100 to 200°C for PU blends and from -20 to 170° for EP blends. Hermetic aluminum pans were used in the Kinetic experiments and nonhermetic aluminum pans, for the Tg determination.

The DSC cell was calibrated by scanning pure indium standard samples which have a known melting point of 156.6°C and a latent heat of melting of 28.4 J/g.

(d) U.V. spectra were recorded on a Perkin-Elmer 552 UV-VIS spectrophotometer from 400 to 190 nm.

(e) I.R. spectra were recorded on a Beckman 4240 I.R. spectrophotometer from 4000 to 200 cm^{-1}. L's were suspended in kBr and pressed into pellet.

APPENDIX 4.3

EQUIPMENT LIST FOR ULTRAFILTRATION MODEL

EQUIPMENT COST CALCULATION

Equipment	Quantity	Unit cost ($)	Installation cost factor	Scaling factor	Fixed capital ($)	Capital charge ($/kg)
1.0 ACID PRECIPITATION						
Lignin extractor	2	50000	1.9	0.6	190000	
Screw press	1	350000	1.6	0.5	560000	
Static mixer	2	5000	1.6	0.4	16000	
Holding tank	1	131756	1.6	N/A	210810	
Extract pump	2	10000	1.9	0.6	38000	
Heat exchanger	2	25000	1.6	0.6	80000	
Vacuum filter	1	150000	1.9	0.6	285647	
Drum dryer	1	185417	2.4	0.4	445000	
Piping	1	50000	1.4	0.2	70000	
Electrical	1	50000	1.4	0.2	70000	
Building	1	100000	1.4	0.2	140000	
				Total =	2105457 FCA	0.013 CRFCA
2.0 UF & ACID PRECIPITATION						
2.1 ULTRAFILTRATION						
Lignin extractor	2	50000	1.9	0.7	190000	
Screw press	1	350000	1.6	0.5	560000	
Micro-filter	1	45000	1.6	0.6	72000	
Surge tank	2	43919	1.9	N/A	166891	
UF pump	2	10000	1.9	0.6	38000	
UF modules	1	2195934	1.6	N/A	3513494	
Heat exchanger	2	15000	1.6	0.6	48000	
Piping	1	30000	1.4	0.2	42000	
Electrical	1	50000	1.4	0.2	70000	
Building	1	100000	1.4	0.2	140000	
				Total =	4840385	0.029
2.2 ACID PRECIPITATION #1						
Static mixer	2	3222	1.6	0.4	10310	
Holding tank	1	43919	1.9	N/A	83445	
Pump	2	6000	1.9	0.6	22800	
Heat exchanger	2	8000	1.6	0.6	25600	
Vacuum filter	1	100000	1.9	0.7	190000	
Dryer	1	127486	2.4	0.4	305967	
Piping	1	30000	1.4	0.2	42000	
Electrical	1	30000	1.4	0.2	42000	
				Total =	722122	0.004
2.3 ACID PRECIPITATION #2						
Static mixer	2	3222	1.6	0.4	10310	
Holding tank	1	43919	1.9	N/A	83445	
Pump	2	6000	1.9	0.6	22800	
Heat exchanger	2	8000	1.6	0.6	25600	
Vacuum filter	1	100000	1.9	0.7	190000	
Drum dryer	1	113629	2.4	0.4	272709	
Piping	1	30000	1.4	0.2	42000	
Electrical	1	30000	1.4	0.2	42000	
				Total =	688864	0.004

EQUIPMENT COST CALCULATION (continued)

Equipment	Quantity	Unit cost ($)	Installation cost factor	Scaling factor	Fixed capital ($)	Capital charge ($/kg)
2.4 ACID PRECIPITATION #3						
Static mixer	2	3222	1.6	0.4	10310	
Holding tank	1	43919	1.9	N/A	83445	
Pump	2	6000	1.9	0.6	22800	
Heat exchanger	2	8000	1.6	0.6	25600	
Vacuum filter	1	100000	1.9	0.7	190000	
Dryer	1	113629	2.4	0.4	272709	
Piping	1	30000	1.4	0.2	42000	
Electrical	1	30000	1.4	0.2	42000	
				Total =	688864	0.004
			Grand total =		6940235	0.042

APPENDIX 4.4

SENSITIVITY ANALYSIS RESULTS FOR ULTRAFILTRATION MODEL

3. PROCEDURE AND RESULTS

3.1 EP-L Polyblends

3.1.1 Materials

(1) An epoxy prepolymer based on DGEBA (Ciba Araldite AY 103) was used without purification. It was cured with a modified aliphatic polyamine (Ciba Hardener HY 956). The materials were reacted according to the manufacturer specifications at a ratio 100 pbw EP to 18 pbw Hardener which is close to the stoichiometric one (AY 103-equivalent weight: 225-238 g/eq.; HY 956 equivalent weight: 47 g/eq.)

The AY 103- HY 956 system is a room temperature or heat curable, solvent free, low viscosity, transparent adhesive optimal for bonding metals, glass, concrete, wood, rubber etc.

(2) The second polymer was either Kraft Lignin, Tomlinite Domtar (TL), unfractionated SEL lignin (UF.F) or < 10K SEL lignin fraction (F.10 K).

The EP-L polyblends were prepared by manually stirring the epoxy prepolymer and the corresponding quantity of L (0 to 20% by weight of polyblend) for two minutes; the equivalent quantity of curing agent was added and the resulting mixture was then stirred for another five minutes.

3.1.2 Adhesive Shear Strength Using Tensile Load for EP, EP-L Polyblends

Single-lap shear joints with aluminum substrates (101.6x25.4x1.6 mm) were used for evaluating the adhesive shear strength by tension loading (ASTM D-1002) with an overlap length of 12.7 mm.

The aluminum substrates were abraded and thoroughly cleaned with acetone. The adhesive mixtures were applied across both sides of the overlap area at a uniform thickness of 0.1 ± 0.03 mm.

Single lap shear specimens prepared with the epoxy system and respective polyblends were subjected to 1 hr cure at 100°C. One series was tested immediately after cooling at room temperature and the other was exposed to temperature cycling for 180 days at 4 cycles/24h in the temperature range -28 to +33°C (720 cycles).

Specimens were tested according to ASTM D-1002 on an Instron testing machine Adhesive shear strength data for the first series of specimens are illustrated in Tab. 1.

Each reported value represents an average of 5-7 determinations. In all the tests failure was in cohesion. As can be seen from Tab. 1 the presence of TL in EP-L polyblends does not improve the adhesive strength. UF. F improves the adhesive strength significantly and even better results were obtained with F.10 k, when at 20% L the adhesive strength has increased with up to 30% in comparison to the adhesive strength of EP control.

3.1.3 Effect of Accelerated Weathering on Adhesive Shear Strength of EP and EP-L Polyblends

Due to accelerate weathering the shear strength of the EP control adhesive and EP-L polyblends decreased (Fig. 1 and 2). The decrease in strength is of about 20% for EP and between 18 and 25% for EP - F.10 k and EP-UF.F polyblends respectively. However the adhesive shear strength for the EP-F.10 K polyblends at a L content superior than 10% is still higher, after accelerated weathering, than that of the EP control sample.

3.1.4 Kinetic Data on the EP Curing in the Presence of L

The mixtures for the evaluation of the kinetic data were prepared in accordance with paragraph 3.1.1 with the following mentions.

- All the materials were weighed accurately on a Sartorius Analytical Balance (accuracy ± 0.1 mg).
- For all the experiments the time from the sample preparation at room temperature until the scanning was kept between 13-15 min.
- The reported data are related to TL and F.10K. As a consequence of UF.F inhomogeneity the results were quite dispersed and unfitted for the Kinetic parameters evaluation.
- Dynamic differential scanning calorimetry (DSC) has been used as the basic method for this investigation, based on the following considerations:
  - the studied system is an accelerated one, and doesn't need an induction period for the formation of intermediate species which markedly accelerates the cross-linking reaction. As can

be seen from Fig. 3, an isothermal experiment done at 70°C occurs with a maximum rate at t=0.

- in the dynamic temperature scan mode, the scan is started at relatively low temperatures compared to reaction temperatures, so that the instrument is in temperature equilibrium at the start of the reaction and the total heat of reaction is more accurately computed for non autocatalized systems.

For thermosets that follow nth order kinetics, the kinetic parameters of curing can be calculated using the Borchardt and Daniel method which gives the following general rate equation:

$$\frac{d\alpha}{dt} = K_T(1-\alpha)^n \qquad (1)$$

where:

α - is the fractional conversion

K_T - is the specific rate constant (s^{-1})

n - is the reaction order, and

t - is the time

The method also assumes that the temperature dependence of the reaction rate follows the expression:

$$K_T = Z \exp^{-E/RT} \qquad (2)$$

where:

Z - is the frequency factor

E - the activation energy (J/mole)

R - the universal gas constant, and

T - the absolute temperature (°K)

So, all the experimental data could be well represented by a three parameter cure model:

$$\frac{d\alpha}{dt} Z \exp\left(-E/RT\right)\left(1-\alpha\right)^{n} \tag{3}$$

$$\text{or} \qquad \ln\frac{d\alpha}{dt} = \ln Z - \frac{E}{RT} + n\ln\left(1-\alpha\right) \tag{4}$$

Eq. (4) is of the general form

$$Z = a + bx + cy \tag{4a}$$

and may be solved with multiple linear regression.

The obtained kinetic parameters are used to calculate curves for fractional conversion as a function of time or temperature according to equation:

$$F\left(t,T\right) = 1 - \left[\left(n-1\right)K\left(T\right)_{t} + 1\right]^{\frac{1}{n-1}} \tag{5}$$

The kinetic data were obtained with a DuPont 1090 Thermal Analyzer - 910 Differential Scanning Calorimeter using the supplied DuPont, Borchardt and Daniel DSC kinetic program.

The DSC kinetics program uses 20 segments of the curve evenly spaced by temperature. The first segment ends at 10% of maximum peak height and the last segment ends at 50% of peak area. A sigmoidal baseline can be used to correct for changes in heat capacity. The values for kinetic parameters n, E and Z are obtained by a multiple regression analysis of this data.

In Fig. 4 are three typical DSC curves, which serve for kinetic data calculations, obtained for EP control and EP-10% TL and F.10K respectively. Arrhenius plots from DSC dynamic scans for cured samples without or with L were straight lines indicating a n^{th} order reaction between cca 54 and 85°C (i.e. the region from 10%, peak height to 50% peak area used by Borchardt-Daniel's Kinetic program). Representative Arrhenius plots are illustrated in Fig. 5.

The Kinetic parameters computed from DSC curves using the DuPont DSC Kinetic program are illustrated in Table 2. As can be seen from the Table 2 the activation energies are close for all the samples with a slight tendency of decreasing with increasing of the L amount. In the EP-TL blends the decreasing of activation energies is higher than in the EP-F. 10 K blends. In both cases L presence does not significantly affect the overall reaction order of the system.

The reactivities of the investigated systems expressed as 80% isoconversion plots in the range of the 40-90°C show, as expected from the kinetic data, a slight decrease of the conversion time for the EP-F.10K polyblends and a quite semnificative decrease for the EP-TL polyblends. Representative isoconversion curves are illustrated in Fig. 6.

The L presence does not significantly affect the EP cure kinetics. However, there are some differences in the kinetic data of the EP curing process due to TL or F.10 K presence. These differences can be attributed to the different degree of reactivity of each type of L.

3.1.5 Tg Determinations for EP and EP-L Polyblends

The Tg of the EP control and EP-L polyblends was determined by DSC according to ASTM D.3418. All the specimens were analyzed after a two week period of cure in laboratory conditions (22°C 40% RH).

Two scans in the same temperature interval were performed for each specimen. The first preliminary thermal cycle was done in order to erase previous thermal history of the sample.

In Fig. 7-9 are presented representative DSC records of the preliminary thermal cycle (first run IR) for the EP-L polyblends.

The characteristic endotherms due to volume relaxation are visible in all the cases. From the DSC curves it can be seen that they do not present any residual exotherm and consequently, the cure appears to be complete. However for the EP-15% TL and EP-

20% TL an exotherm is starting at around 140 and 120°C respectively depicting a post curing process during the first DSC run.

The Tg values were obtained on the record of the second DSC scan (second run - IIR) at intercepts between the extrapolated base line preceding the endothermic shift and the tangent drawn at the flexus point of the signal. Du Pont Analysis Program - Interactive DSC V2.0 was utilized for Tg calculation.

The Tg data are presented in Table 3 and represent at least an average of three determinations. In Fig. 10-12 are illustrated representative second DSC scans for the EP-L polyblends. The EP's Tg position is figurate, as well as the L's Tg position in those polyblends in which it is visible.

In parallel the L's Tg were determined in the same way. The results are illustrated in Figure 13-14 which represent the record of DSC second scan. Also in Fig. 13-14 it can be seen the mode of Tg calculation by the Interactive Data Analysis Program.

As can be seen from Fig. 10-12 and Table 3, the L presence does not significantly affect the EP's Tg. A slight Tg increasing takes place only in the presence of TL and the increasing can be correlated with the L content. L seems to be miscible in all the polyblends since they exhibit a single Tg characteristics of a monophasic system. Exception are the EP-15 UF.F and EP-20 UF.F polyblends. For EP-15 and 20% UF.F a second Tg is located in the temperature region for L molecular motions and this discloses the immiscibility of those polyblends.

3.1.6 Extractibility of L from EP-L Polyblends

For determining the extractability of L from EP-L polyblends, a suitable amount of polyblend powder (to contain about 4 mg L) was weighed accurately on a Sartorius 4501 microbalance (accuracy of ± 0.005mg), placed in an Erlenmayer flask with 20 ml dioxane-water 9:1 (by volume) then refluxed under constant stirring for 10 hrs. The indissolved material was quantitatively filtered off and washed with dioxane-water in a 50 ml volumetric flask. The filtrate was then diluted to the mark and thoroughly shaken.

For UV analysis, a 10 ml aliquout was diluted to 25 ml with the same solvent. The obtained solution was analyzed in UV from 400 to 190 nm in 1-cm silica cells.

First the L characterization in U.V. was done. The UV absorbtion spectra of L solutions in dioxane water show a characteristic maximum at 277 nm. The absorbance at 277 nm was used to establish the calibration curve for L in the dioxane-water solution. TL characteristics absorptivity was found to be 22.07 A.1. $g.^{-1}$ cm^{-1} and UF.F 17.78-A.1.g^{-1} cm^{-1}. These absorptivity values were used to determine the L concentration in EP-L polyblend solutions. The solutions were scanned versus a corresponding blank solution of EP control sample prepared in the same way as the EP-L polyblend samples. In all cases, the absorbance values recorded are averages of three determinations. The degree to which L is chemically bonded to the EP network was calculated from the L concentration in EP-L polyblend solutions after extraction. The percentage of L bonded to EP network is illustrated in Fig. 15.

3.2 PU-L Polyblends

3.2.1 Materials

To obtain a formulation of a flexible PU with good deformation properties even at low temperatures, characteristic for a joint sealant, a two component PU system was used.

The isocyanate component was a solvent free highly molecular weight aromatic prepolymer, Desmodur E 14 (Bayer), with a NCO content of 3,5% and an equivalent weight of 1200.

The polyolic component was a branched polyether, Desmophen 1920 D (Bayer) with an OH content of 0.85% and an equivalent weight of 3200.

A dynamic calorimetric measurement from 0 to 200°C with a heating rate of 5°C/min and an isothermal one at 130°C for 60 min., showed that the reactivity of the system is very low in terms of curing time. Both measurements were done with a Du Pont 1090 Thermal Analyser for a mixture isocyanate-polyol corresponding to a NCO:OH ratio of 1:1. Consequently the curing time was controlled by catalysts - organic metal compounds-, respectively a mixture of calcium and lead octate. Their concentration was established for a pot life of 20-30 minutes.

In order to increase the flexibility of the system, a plasticiser, butyl benzene phthalate, was also incorporated in the formulation.

To avoid the reaction of the isocyanate component with atmospheric moisture, a water absorbent product was added in the mixture; Baylith Paste (Bayer), was used for this purpose in proportion of 5-7% by weight. This paste is an alkali alumino silicate 50% in castor oil. Thus the amount of OH groups if castor oil was also taken in account for PU formulation.

All the materials are commercial products and were used as received.

3.2.2. Tensile Properties of PU-L polyblends

The two-part polyurethane based sealant was blended with various amounts of TL and UF.F. to produce a series of tensile specimens conforming to ASTM D412 (Die "D"). These blends were compared to a conventionally formulated sealant containing a silica/TiO_2 filler.

The blending procedure was carried out in a controlled nitrogen atmosphere such that the potential for moisture absorption by the particulated matter, and the reaction of moisture with the polyurethane components was kept to a minimum. All particulate matter used in this study was dried in a forced-air oven at 105°C for at least two hours.

Hence, weight percentages of 5, 10, 15 and 20 TL, UF.F. or 30% silica/TiO_2, were blended with the polyol fraction of the two-part sealant. The blend was hand mixed until a uniform texture was obtained, after which sufficient isocyanate was added to obtain a stoichiometric ratio of 1.02:1 NCO:OH. Finally, an appropriate amount of catalyst was added, and the entire blend was hand stirred for two minutes to insure a thorough dispersion of this fraction within the mixture.

Each batch formulation consisted of casting four tensile specimens, having nominal dimensions of 3 x 5 x 200 mm (1/8 x 1 x 4 in.). These were allowed to cure at room temperature within the controlled atmosphere for at least nine hours and after unmoulding, for two weeks in laboratory conditions (22°C, 40% RH). Specimens were then cut to the designated shape by pressing a suitable die into the cast stock.

The specimens were tested on an Instron Universal Testing Machine according with the procedure described on the point 2a. The tensile test results are indicated in Tab. 4.

3.2.3 Effect of Accelerate Weathering on the Tensile Properties of PU and PU-L Polyblends

Set of specimens prepared in the same conditions as those described at paragr. 3.2.2 were subjected to accelerated weathering for 93 days - 4 cycle/day i.e. 371 cycle between -an average of -18 to + 33°. The thermal shock due to cycling has not a significant effect on the tensile properties of both PU-TL and PU-UF.F polyblends, as can be seen in the Table 5.

3.2.4 Tg Determinations for PU and PU-L Polyblends

The Tg of the PU control ad PU-L polyblends was analyzed by DSC according to ASTM 3418. All the specimens were cured at room temperature within the controlled atmosphere for at least 9 hours and for two weeks in laboratory conditions (22°C, 40% RH).

In the case of PU and PU-L polyblends the Tg was determined in the first scan, as the endotherms due to volume relaxations were absent in the first scan. This was expected since the PU crosslinking is not an exothermic process and in addition the delay time between sample preparation and scanning was relatively short.

The thermal behaviour of PU elastomers is characterized by several thermal transitions arriving from hard (urethane) segments and soft (polyether) segments.

Important transitions found in most PU elastomers include:

- Glass transition of the soft segments between -80 and - 10°C
- Microcrystalline melting of the soft segments between 10 and 20°C
- Short range ordering of hard segments between 60 and 100°C
- Long range ordering of hard segments between 120 to 190°C.

In PU system the following transitions were identified:

- Tg of the soft segments at around - 52°C
- Short range ordering of the hard segments at around 77°C
- Long range ordering of the hard segments at around 164°C

The Tg of the soft segments were computed from the DSC record in the same way as for the EP's Tg. The DSC thermal events arriving from the hard segments motions are much less intense than those of the soft segments. Consequently their position was determined manually as the intersection between tangent drawn at the flexus point and base line.

In Figure 16A and B are illustrated the Tg's of control PU and PU-TL polyblends and in Fig. 17A and B the Tg's of control PU and PU-UF.F polyblends.

For the PU-UF.F polyblends L presence does not affect the Tg's of hard or soft segment. The polymers seem to be miscible as the L's Tg is not detectable (Fig. 17 B).

In the case of PU-TL polyblends as a consequence of L presence, temperature of the short range ordering of hard segments is raised with about 10°C. In addition, the polymers looks like unmiscible since a typical heat capacity jump in the L transition region is visible and quite well defined (Fig. 16B).

All these data are also illustrated in Table 6 were the average of at least three determinations are presented.

3.2.5 Extractibility of L from PU-L Polyblends

L extractibility from PU-L polyblends was performed in the same way as for EP-L polyblend. The L solutions after extraction were scanned in UV versus a corresponding blank solution of PU control sample. The percentage of L bonded to PU, calculated from the L concentration PU-L solutions after extraction is illustrated in Fig. 18.

CONCLUSION

Presented experimental data indicated that SEL lignins could be successfuly utilized in polyblends formulation with an EP adhesive (Ciba Geigy AY 103 - HY 956).

When compared with the EP control, the adhesive strength in shear of the EP-20% U.F. F and EP-20% F. 10k disclosed superior performance i.e. about 15% and 30% higher respectively. Moreover, the adhesive shear strength for the EP-F. 10k polyblends at a L content superior than 10%, after accelerated wheathering is still higher than that of the EP control.

In the same polyblends TL presence has little effect on the adhesive shear strength.

In the PU-L studied systems (Desmodur E14 - Desmophen 1920D) the effect of L's upon the mechanical properties is less obvious than in EP-L polyblends.

The rest of the data indicated that each type of L participate in a particular manner in polyblends morphology. This fact can be explained by some differences in their chemical structure. These differences can be easily observed in the L's infrared spectra (Fig. 19).

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Table 6 Tg's values for Pu-L polyblends determined by DSC

TABLE 1 - Adhesive Shear Strength of EP, EP-L Polyblends Determined According to ASTM D-1002

Specimen Type	Shear Strength (MPa)				
	EP-0%L (control)	EP-5%L	EP-10%L	EP-15%L	EP-20%L
F.10k	18.6	18.9	23.5	22.4	24.0
UF.F	18.6	19.6	20.7	21.5	21.4
TL.	18.6	19.0	19.2	19.0	19.0

TABLE 2 - Kinetic Parameters from DSC curves as function of L content

No.	Specimen Type	Reaction Order	Activation Energy J/mol.	Log z	Heat of Reaction J/g
1	EP control	1.48	71.1	9.47	336.0
2	EP-5% TL	1.43	70.1	9.30	323.0
3	EP-10% TL	1.22	66.5	8.75	310.0
4	EP-15% TL	1.15	64.0	8.42	294.0
5	EP-20% TL	0.92	60.0	7.83	270.0
6	EP-5% F.10k	1.46	69.1	9.16	328.5
7	EP-10% F.10k	1.36	68.8	9.06	312.5
8	EP-15% F.10k	1.15	66.1	8.70	284.7
9	EP-20% F.10k	0.97	63.1	8.36	256.5

TABLE 3 **Tg's values for EP-L Polyblends determined by DSC**

L Content %	Tg °C					
	TL		UF.F		F. 10k	
	1st Tg	2nd Tg	1st Tg	2nd Tg	1st Tg	2nd Tg
5	52.1	-	50.9	-	50.2	-
10	52.2	-	51.7	-	50.5	-
15	54.2	-	52.6	133.8	53.1	-
20	60.2	-	53.7	135.0	50.9	-

NOTE: The average of EP Tg was 50.3°C

TABLE 4 - Tensile Properties of PU, PU-L Polyblends Determined According to ASTM D-412

No.	Specimen Type	Tensile Properties			
		Stress of Rupture kPa		Elongation of Rupture %	
		Average[*]	Coeffic of variations %	Average	Coeff. of variations
1	PU control	603	7.3	122.4	1.6
2	PU-5% TL	595	5.0	91.5	15.5
3	PU-10% TL	577	15.4	86.5	27.2
4	PU-15% TL	687	4.11	88.0	12.1
5	PU-20% TL	720	5.0	90.0	12.1
6	PU-5% UF.F	545	3.7	86.0	9.6
7	PU-10% UF.F	587	3.0	82.6	11.0
8	PU-15% UF.F	630	3.4	78.2	7.8
9	PU-20% UF.F	642	3.0	73.9	8.0

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[*] Each figure represents the average of 4 tests

TABLE 5 - Effect of the Accelerated Wheathering on the Tensile Properties of PU - L Polyblends

No.	Specimen Type	Tensile Properties			
		Stress of Rupture kPa		Elongation of Rupture %	
		Average**	Coeffic of variations %	Average	Coeff. of variations
1	PU control	613	5.3	132.8	5.2
2	PU-5% TL	574	8.2	98.2	15.0
3	PU-10% TL	645	9.5	93.6	18.0
4	PU-15% TL	645	5.7	84.4	12.0
5	PU-20% TL	662	4.4	75.7	12.0
6	PU-5% UF.F	564	2.2	96.3	5.0
7	PU-10% UF.F	555	2.1	77.9	9.0
8	PU-15% UF.F	613	2.7	74.6	9.1
9	PU-20% UF.F	600	5.0	68.3	2.1

** Each figure represents the average of 4 tests

TABLE 6 - Tg's values for PU-L Polyblends determined by DSC

No.	L content %	PU - Type							
		PU - UF.F				PU - TL			
		PU Tg°C			L Tg°C	PU Tg °C			L Tg °C
		1st Tg	2nd Tg	3rd Tg		1st Tg	2nd Tg	3rd Tg	
1	0	- 52.0	76.5	165.4	-	- 52.0	76.5	165.4	-
2	5	- 51.6	72.8	166.5	-	NO	DATA		
3	10	- 51.8	73.5	168.5	-	- 51.3	86.9	165.4	126.0
4	15	- 51.8	74.3	166.8	-	NO	DATA		
5	20	- 52.0	70.7	166.5	-	- 51.9	86.5	163.8	128.4
6	100	-	-	-	127.3	-	-	-	127.7

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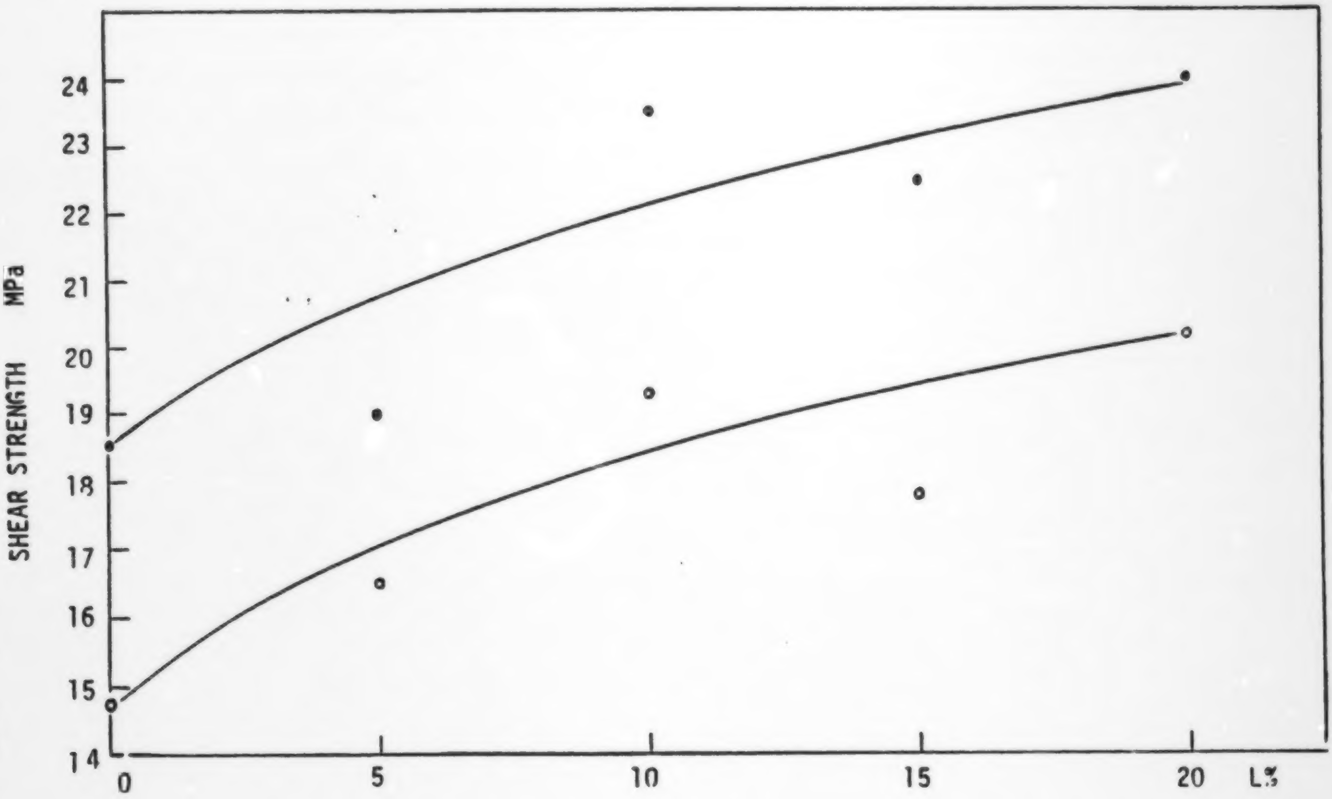


Figure 1 Adhesive shear strength (by tension loading) for the EP control and EP-UF.F polyblends

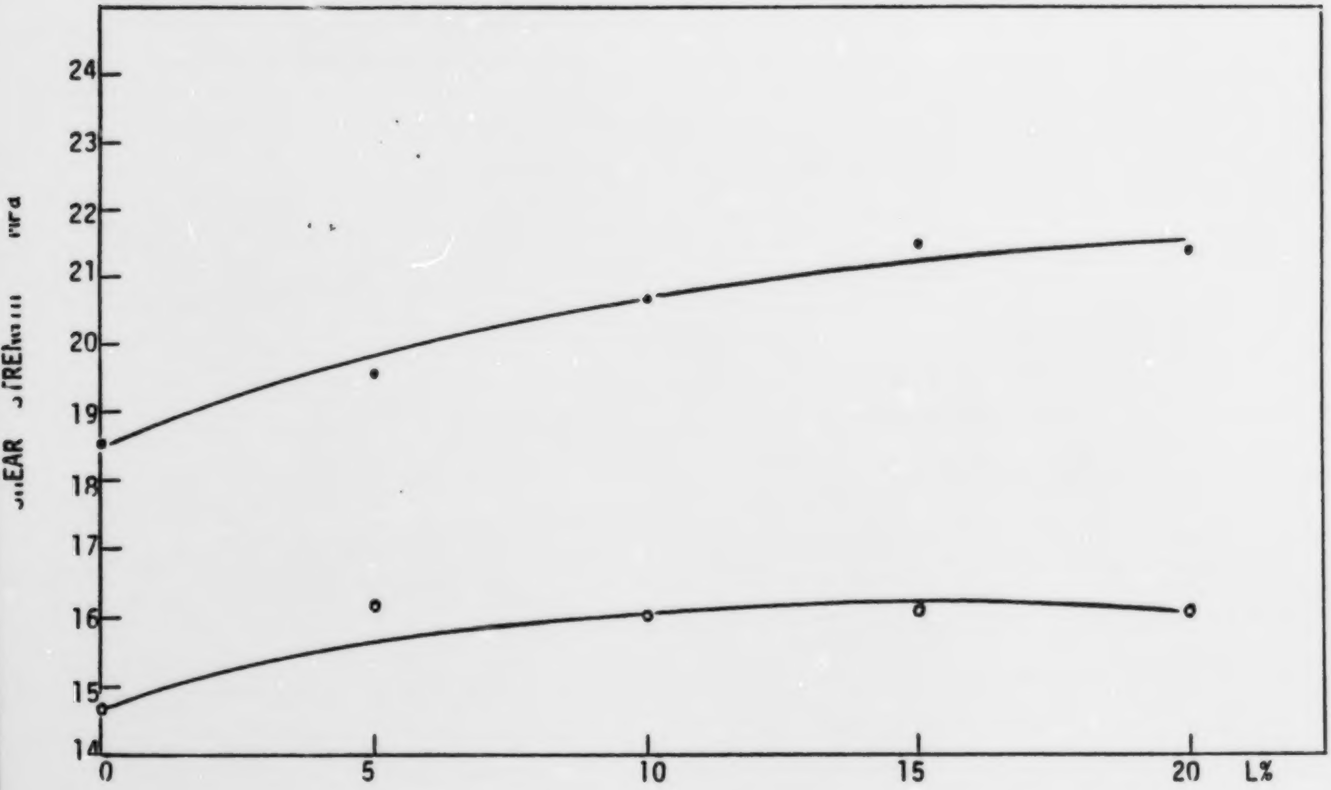


Figure 2 Adhesive shear strength (by tension loading) for the EP control and EP-F.10K polyblends

Figure 3 Isothermal DSC curve for EP prepolymer-hardener at 70°C

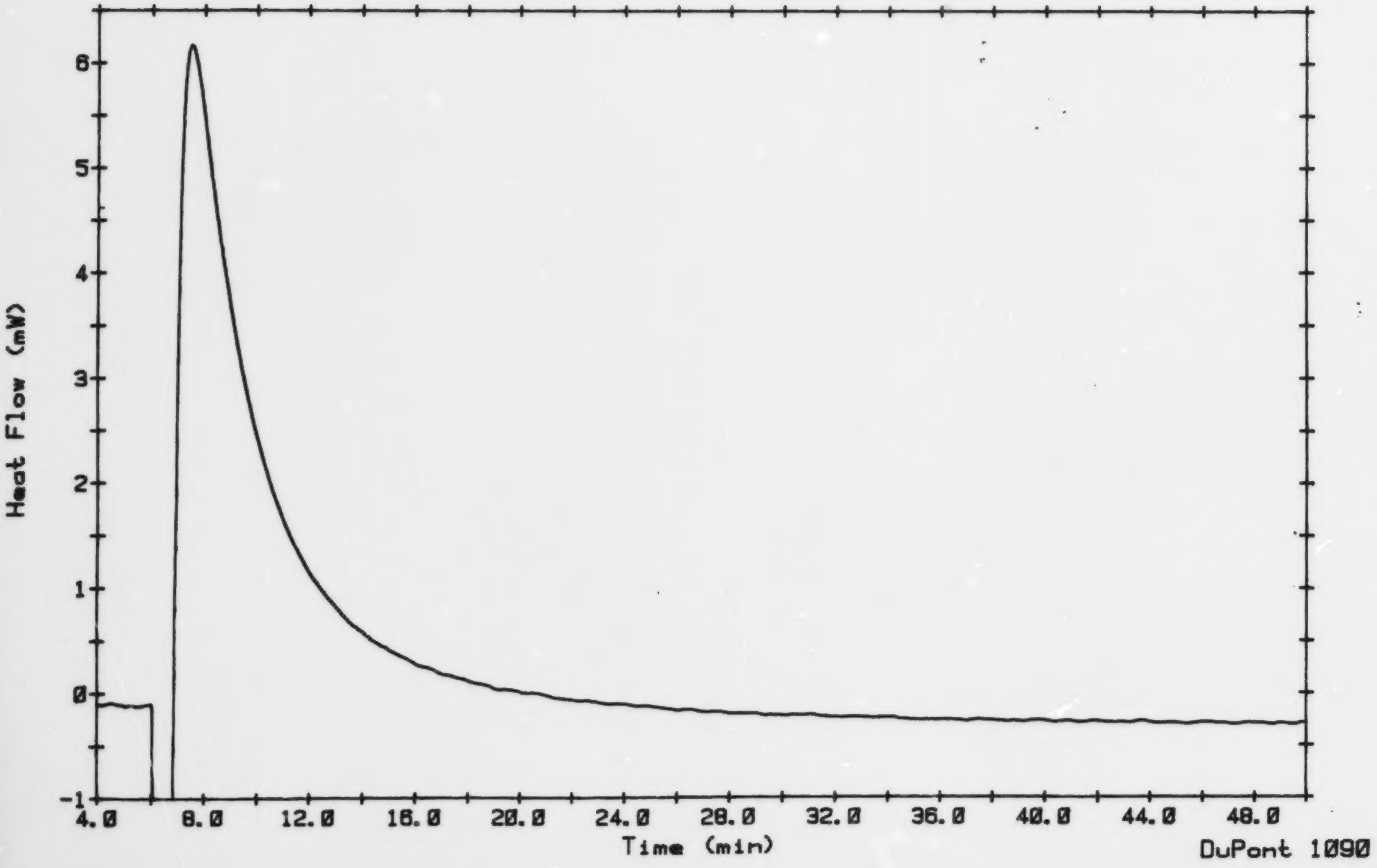


Figure 4 Typical DSC curves for the determination of the curing kinetic parameters

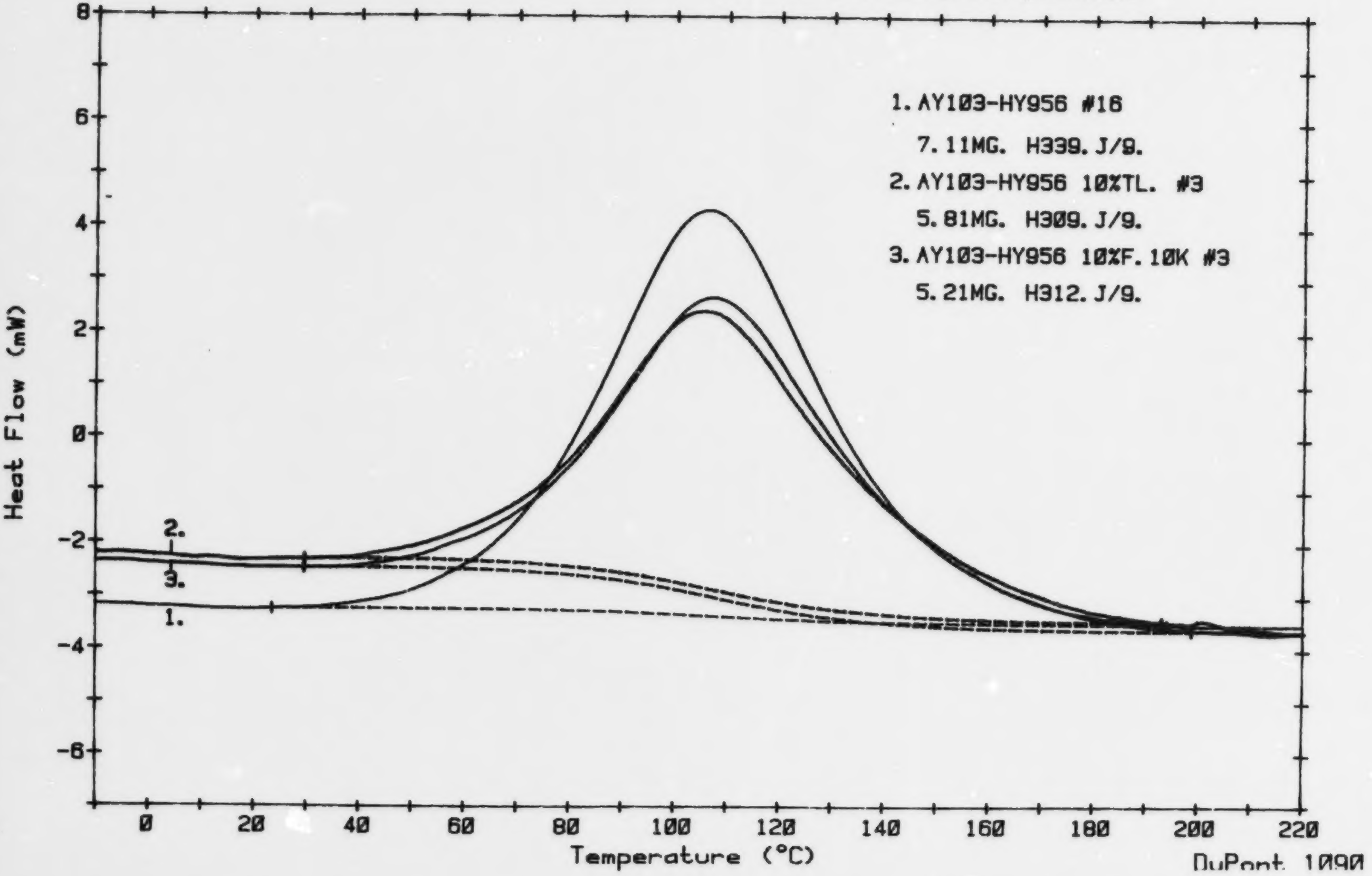


Figure 5 Representative Arrhenius plots

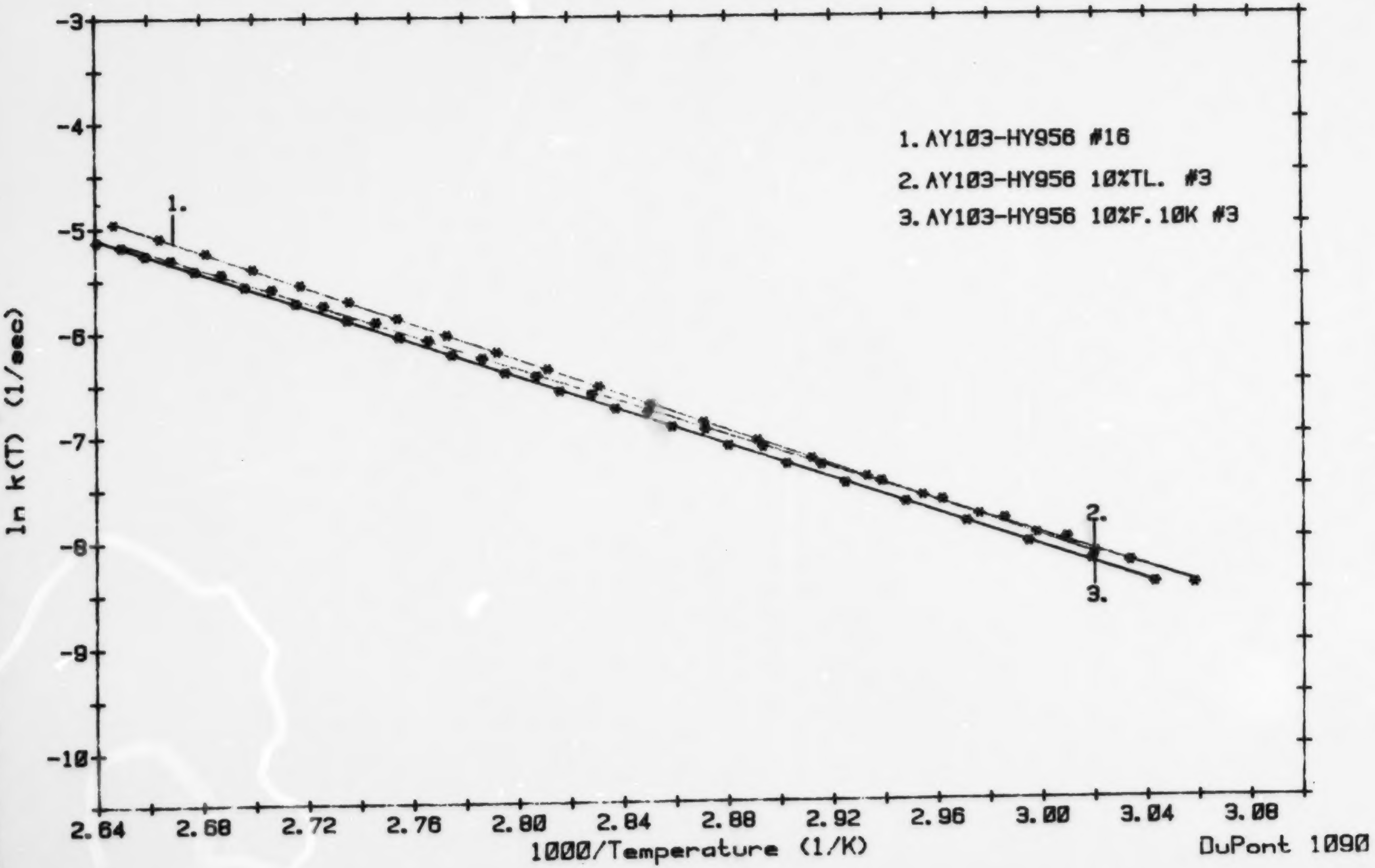


Figure 6 Relative reactivity as function of type of L (10% L in polyblend, temperature range 40-90°C)

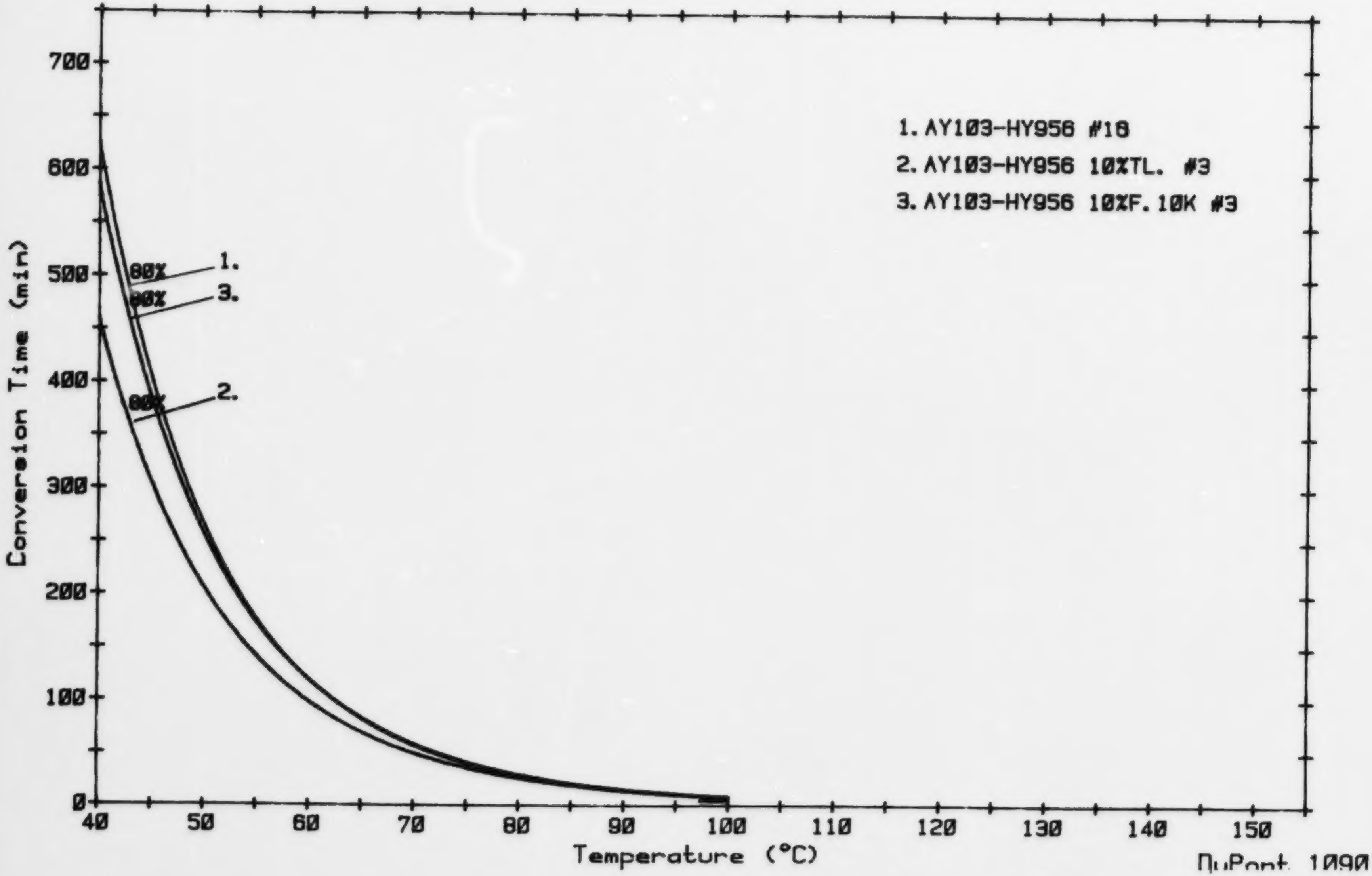
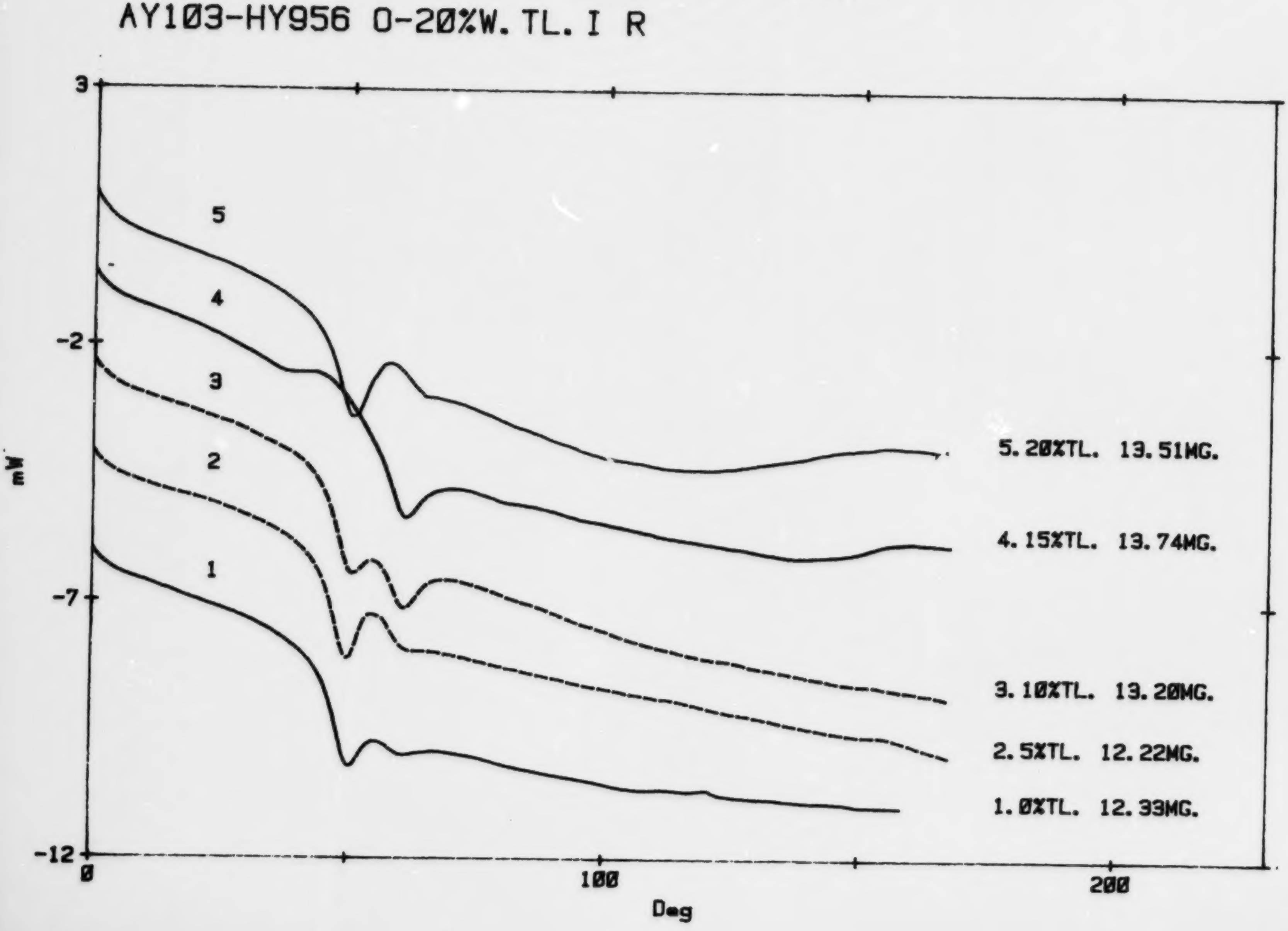


Figure 7 DSC first scan for the EP-TL polyblends



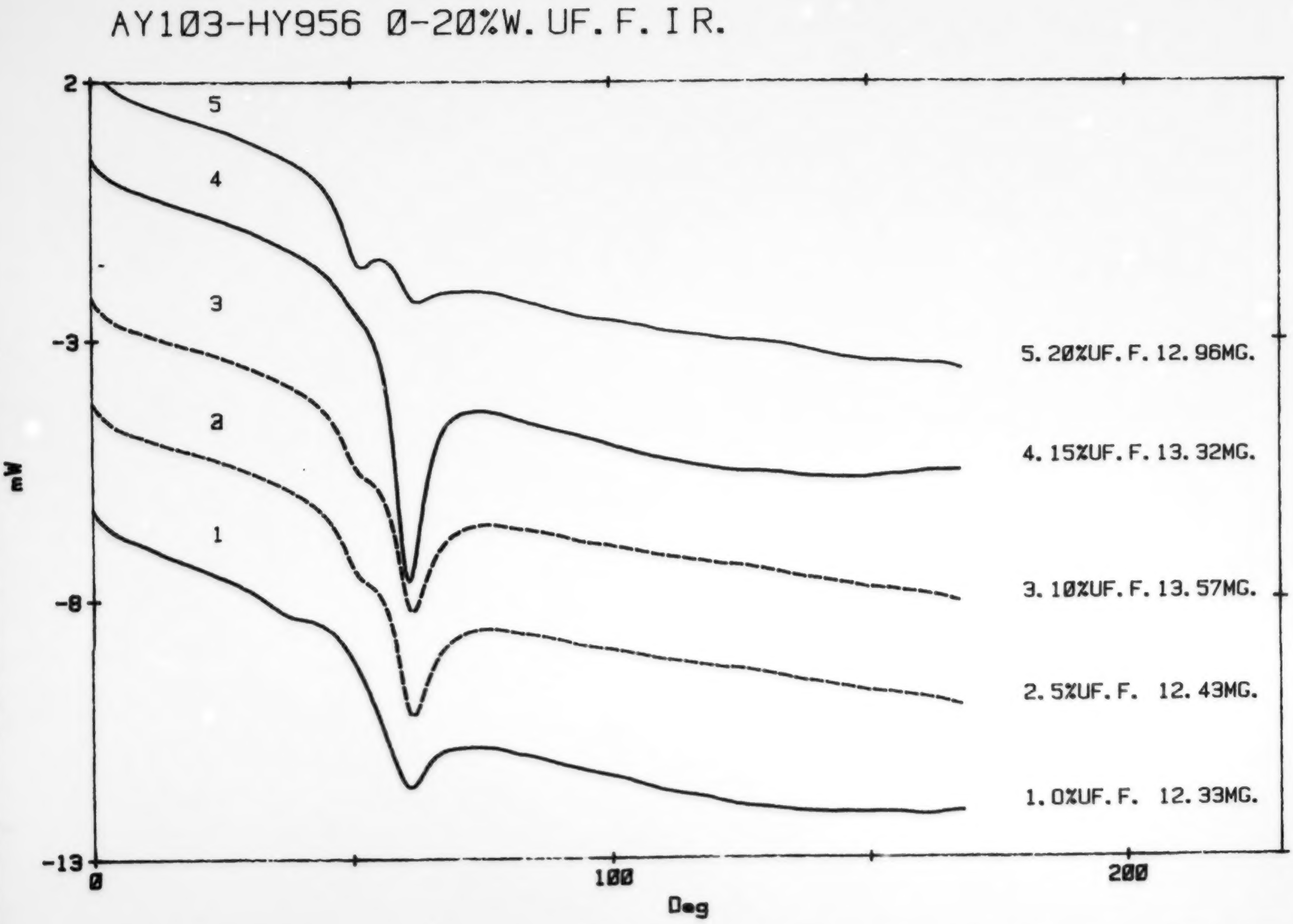


Figure 8 DSC first scan for the EP-UF.F polyblends

Figure 9 DSC first scan for the EP-F. 10 K polyblends

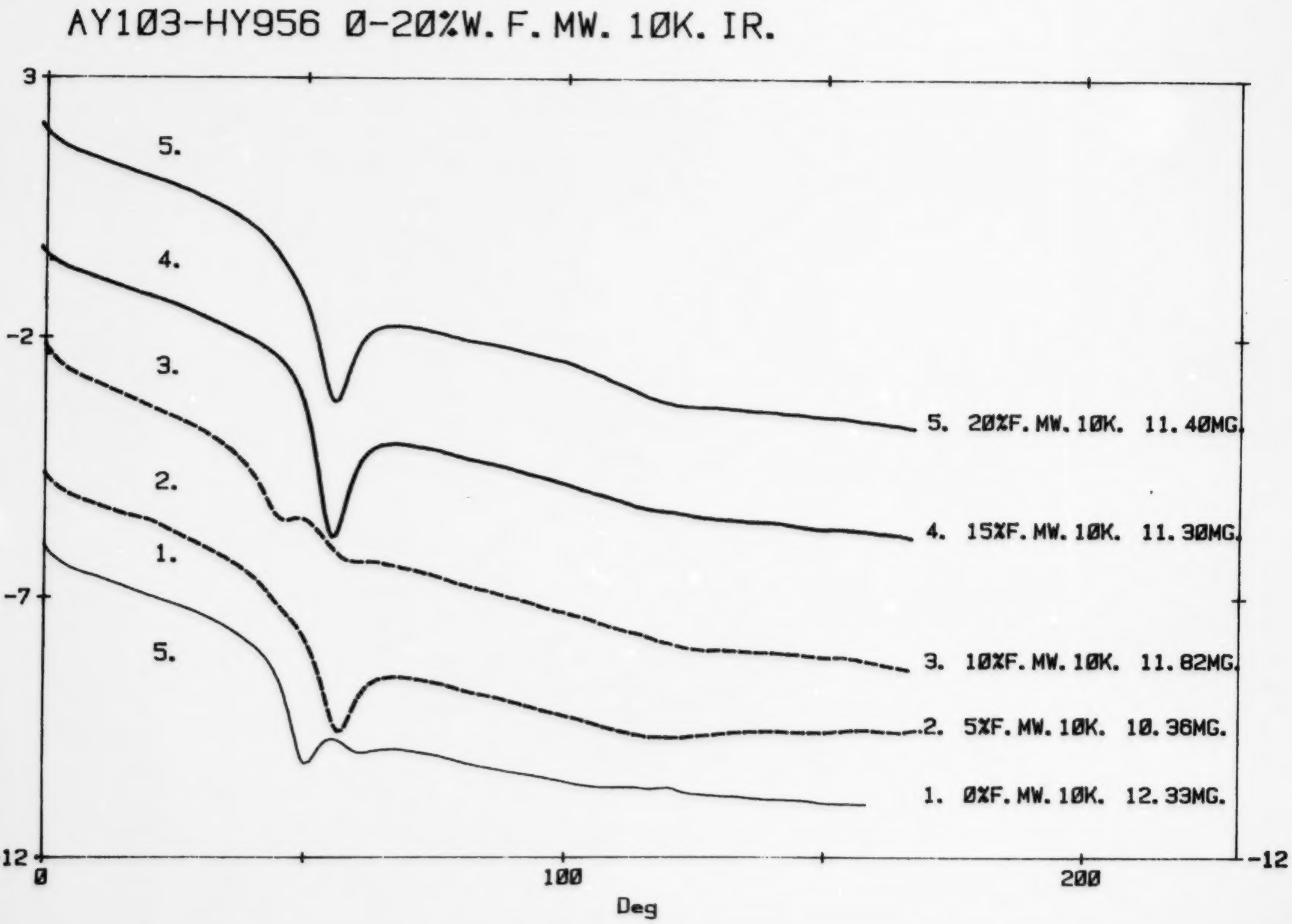
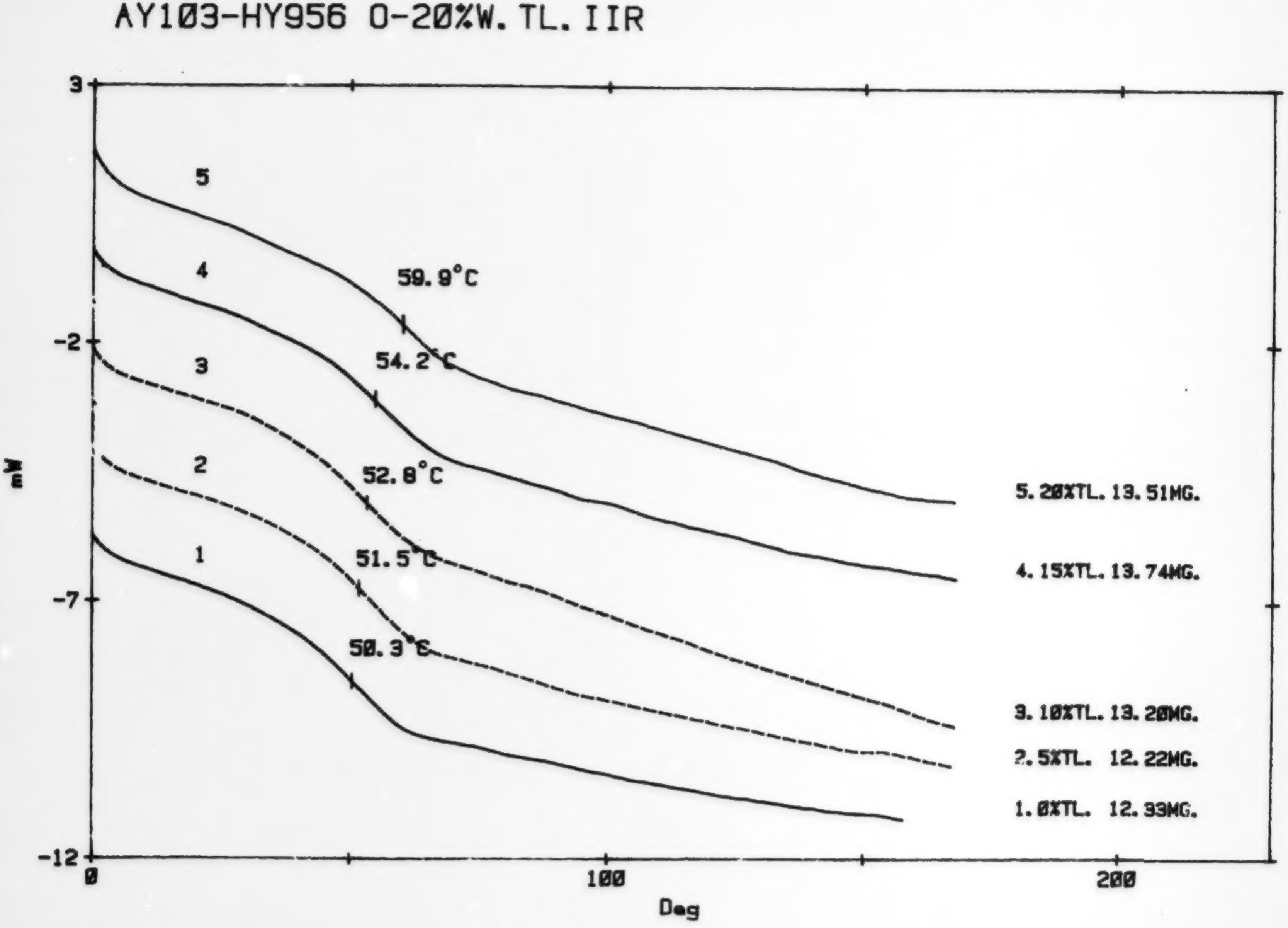


Figure 10 DSC second scan for EP-TL polyblends



AY103-HY956 0-20%W. UF. F. I IR.

Figure 11 DSC second scan for EP-UF.F. polyblends

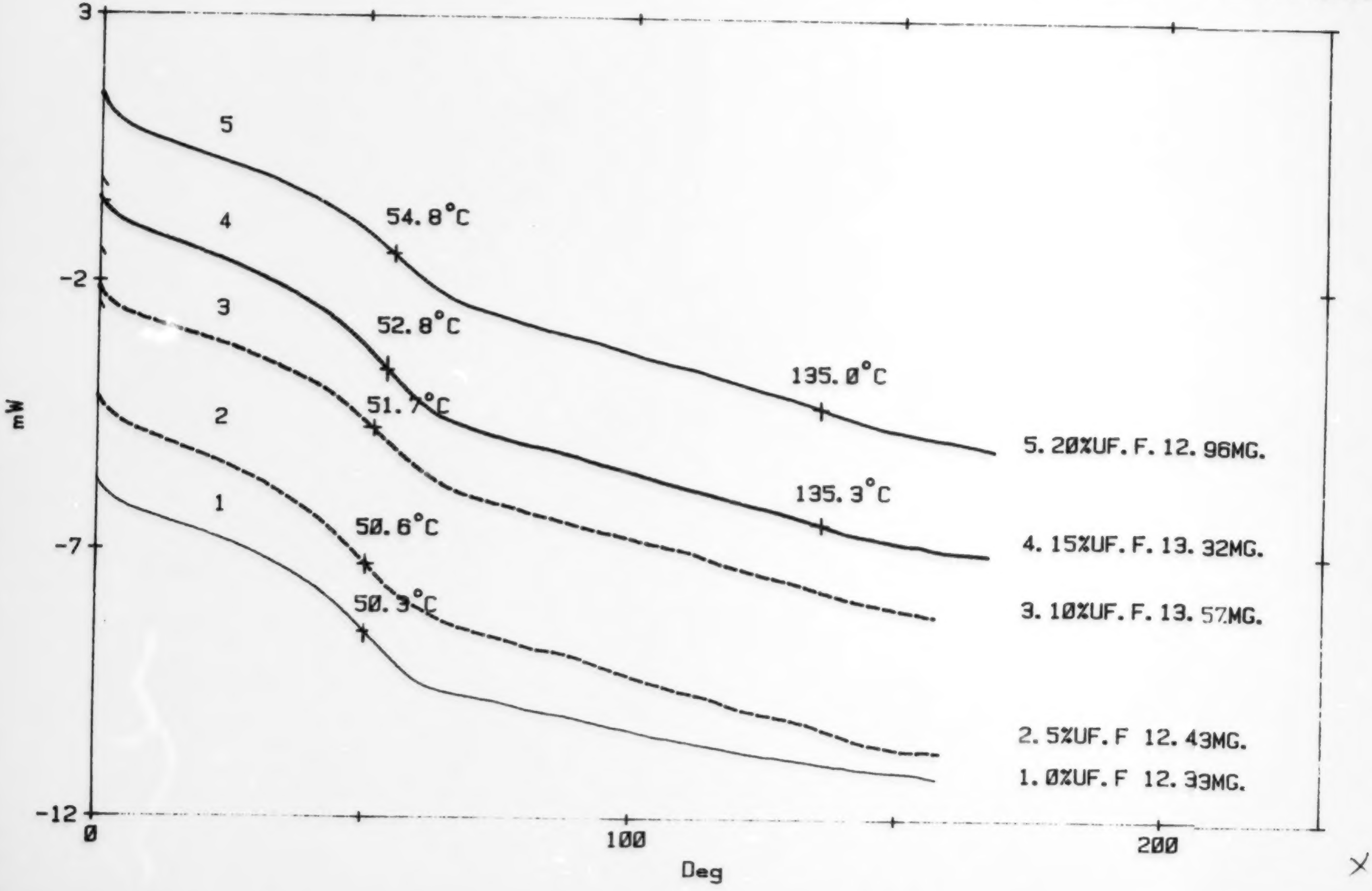


Figure 12 DSC second scan for EP-F. 10K polyblends

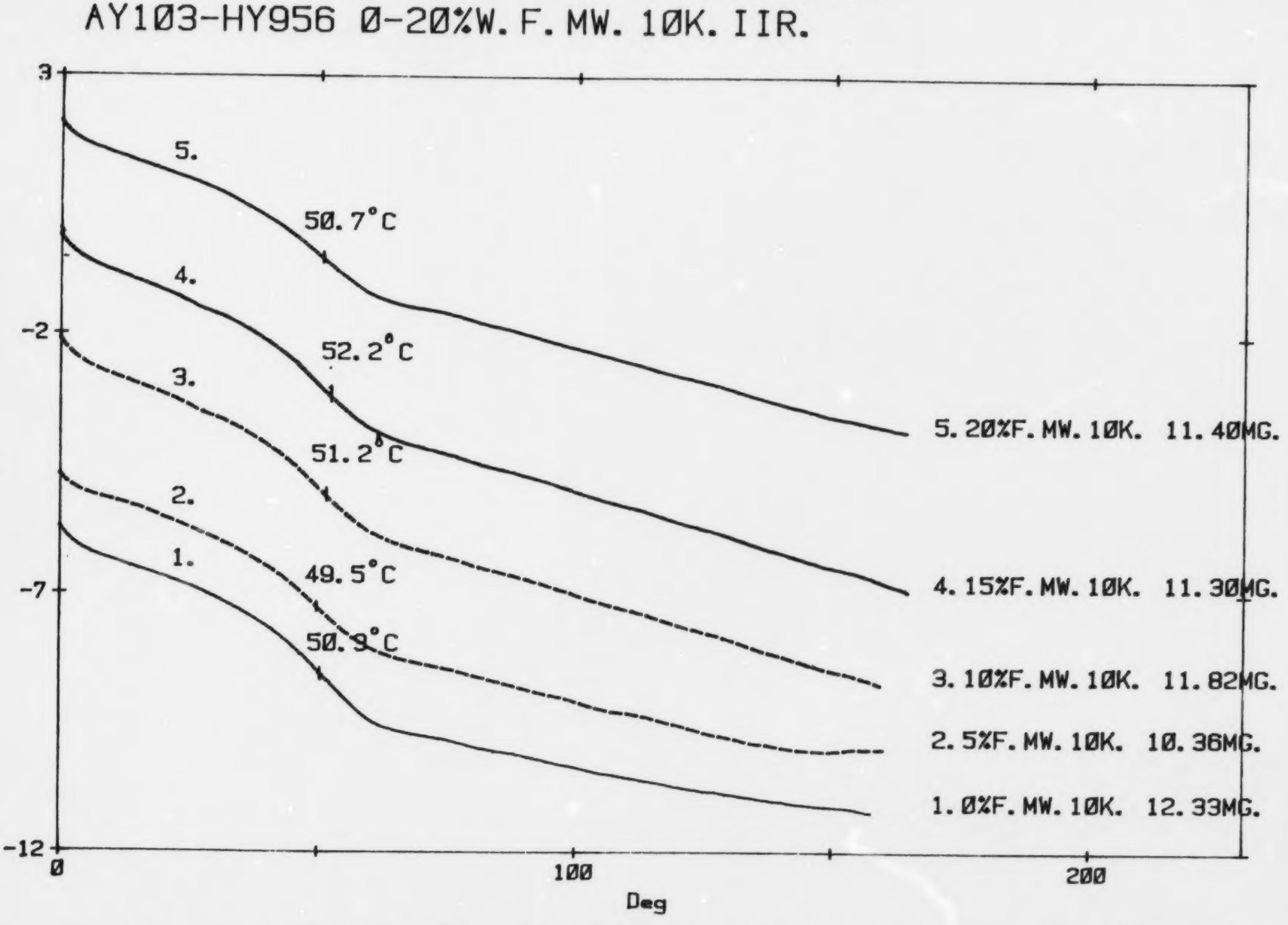


Figure 13 DSC second scans for TL

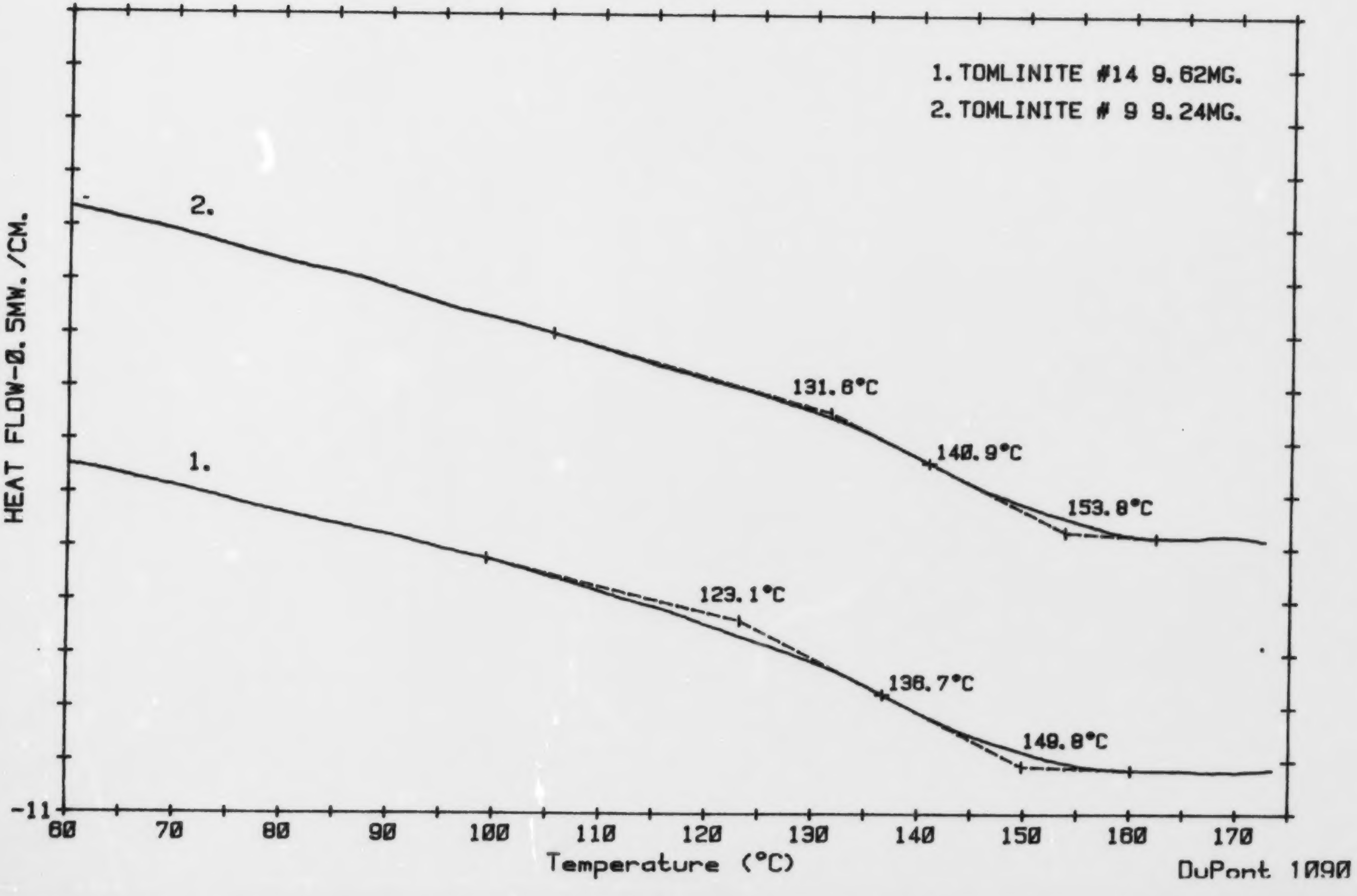


Figure 14 DSC second scans for UF.F and F.10K

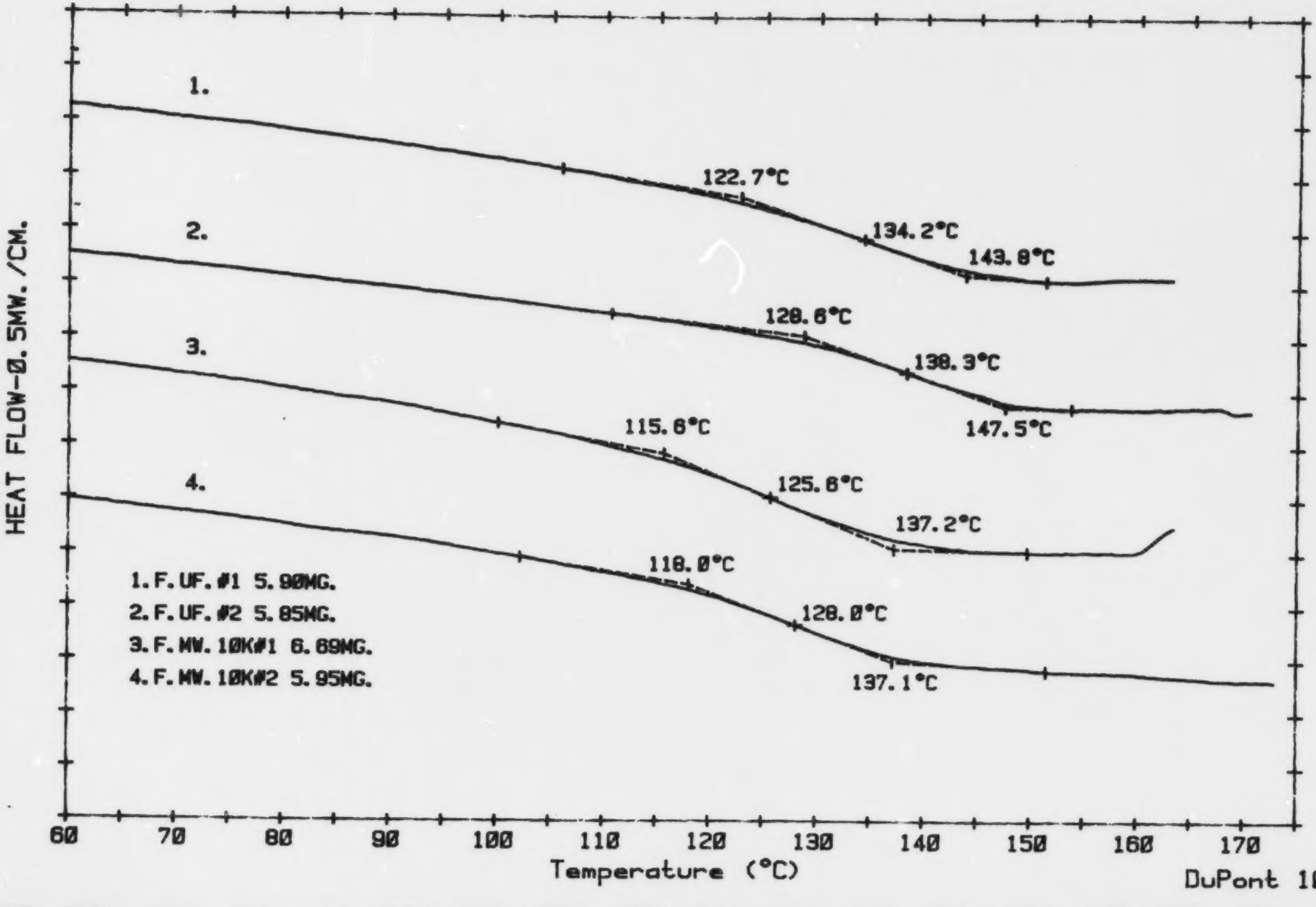


Figure 15 Extractibility of L from the EP-L polyblends

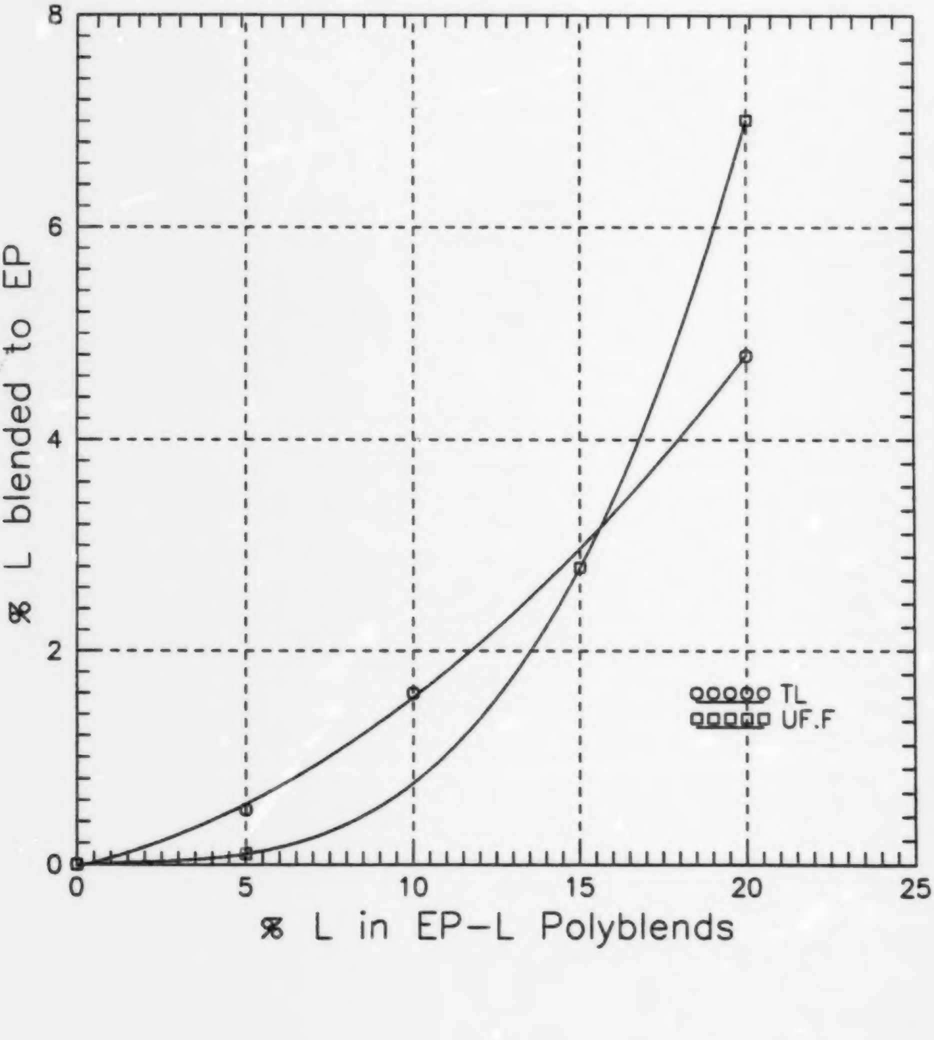


Figure 16A- DSC scans for PU-TL polyblends

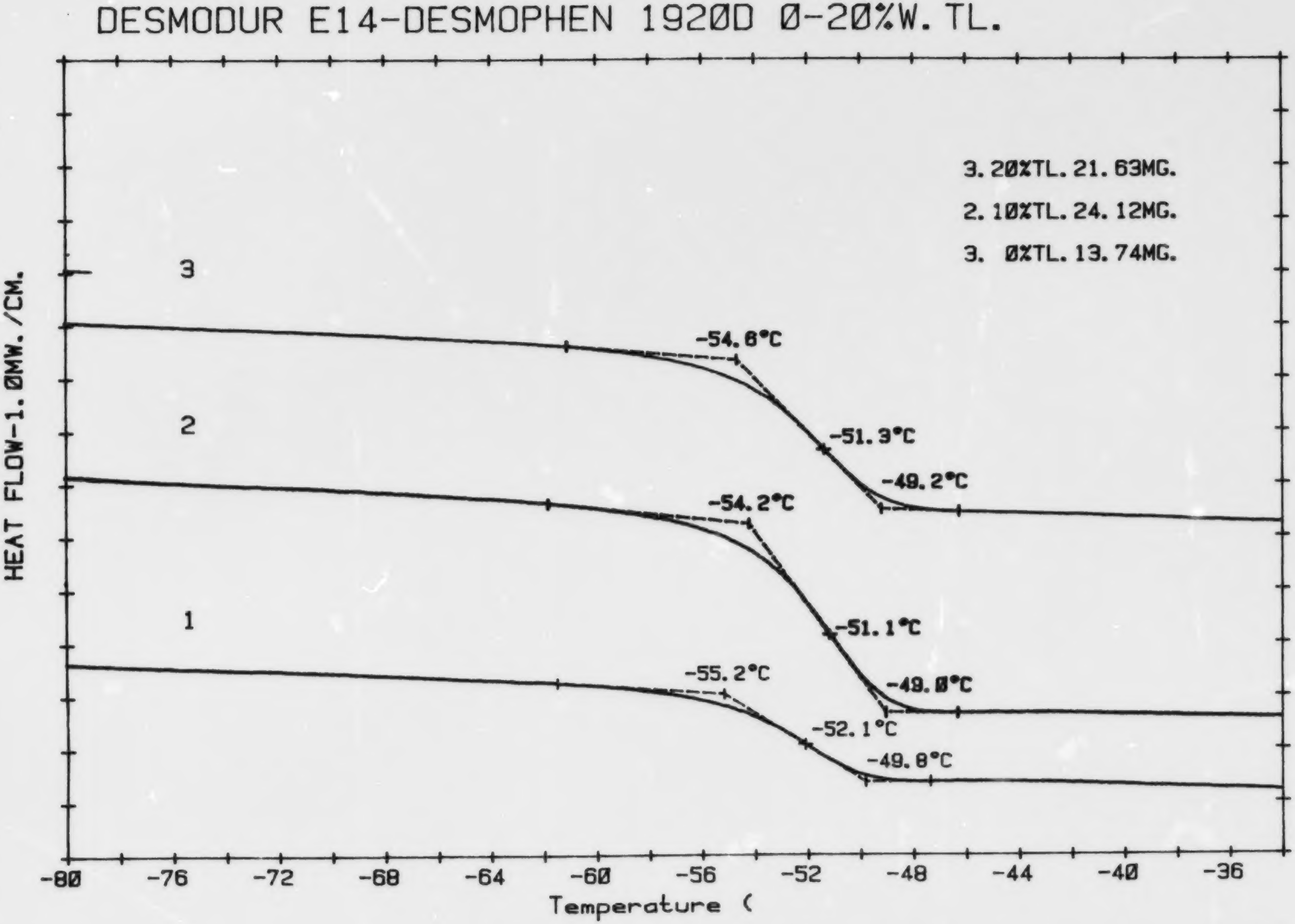


Figure 16 -B DSC scans for PU-TL polyblends

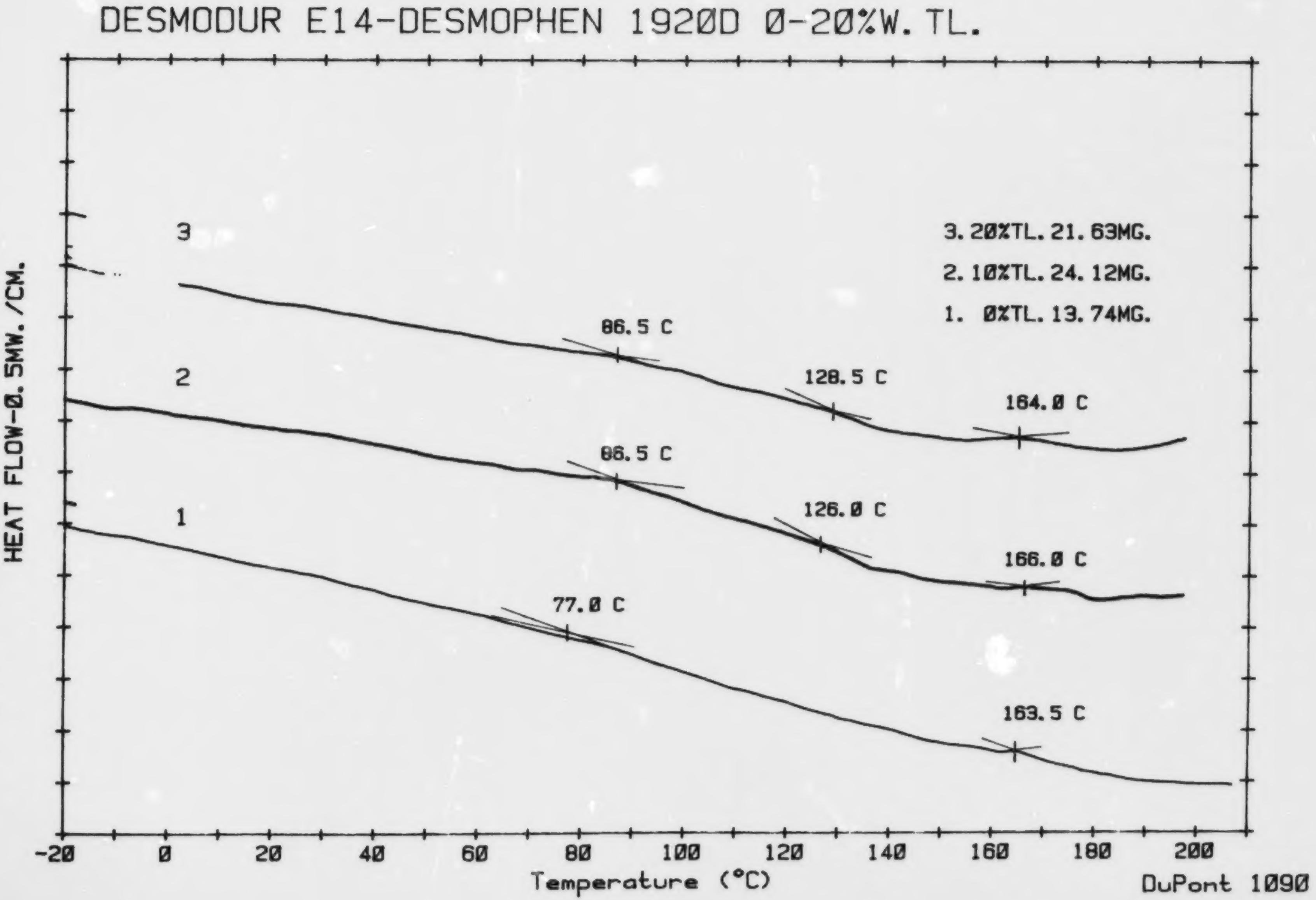


Figure 17A- DSC scans for PU-UF.F. polyblends

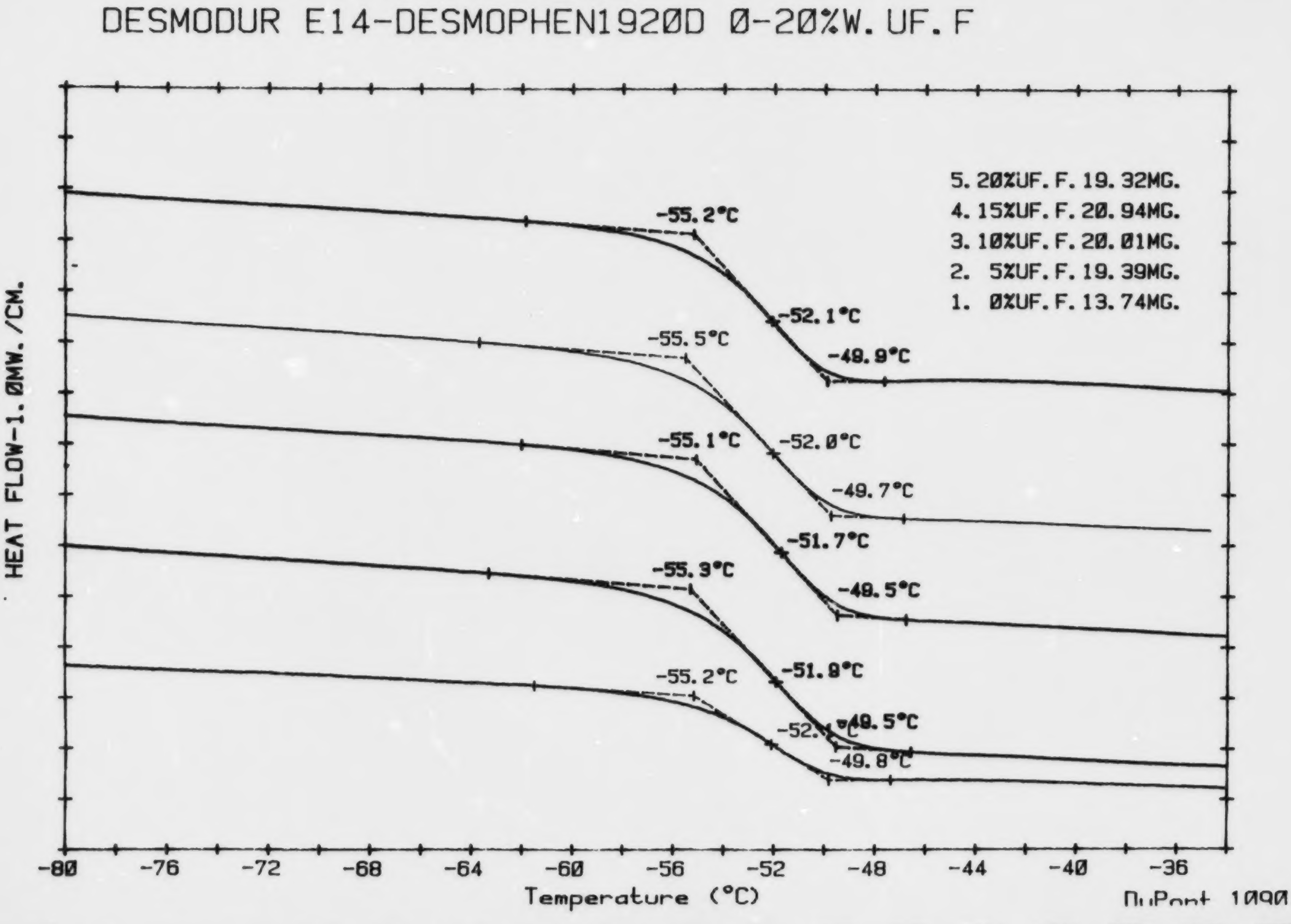


Figure 17 -B DSC scans for PU-UF.F. polyblends

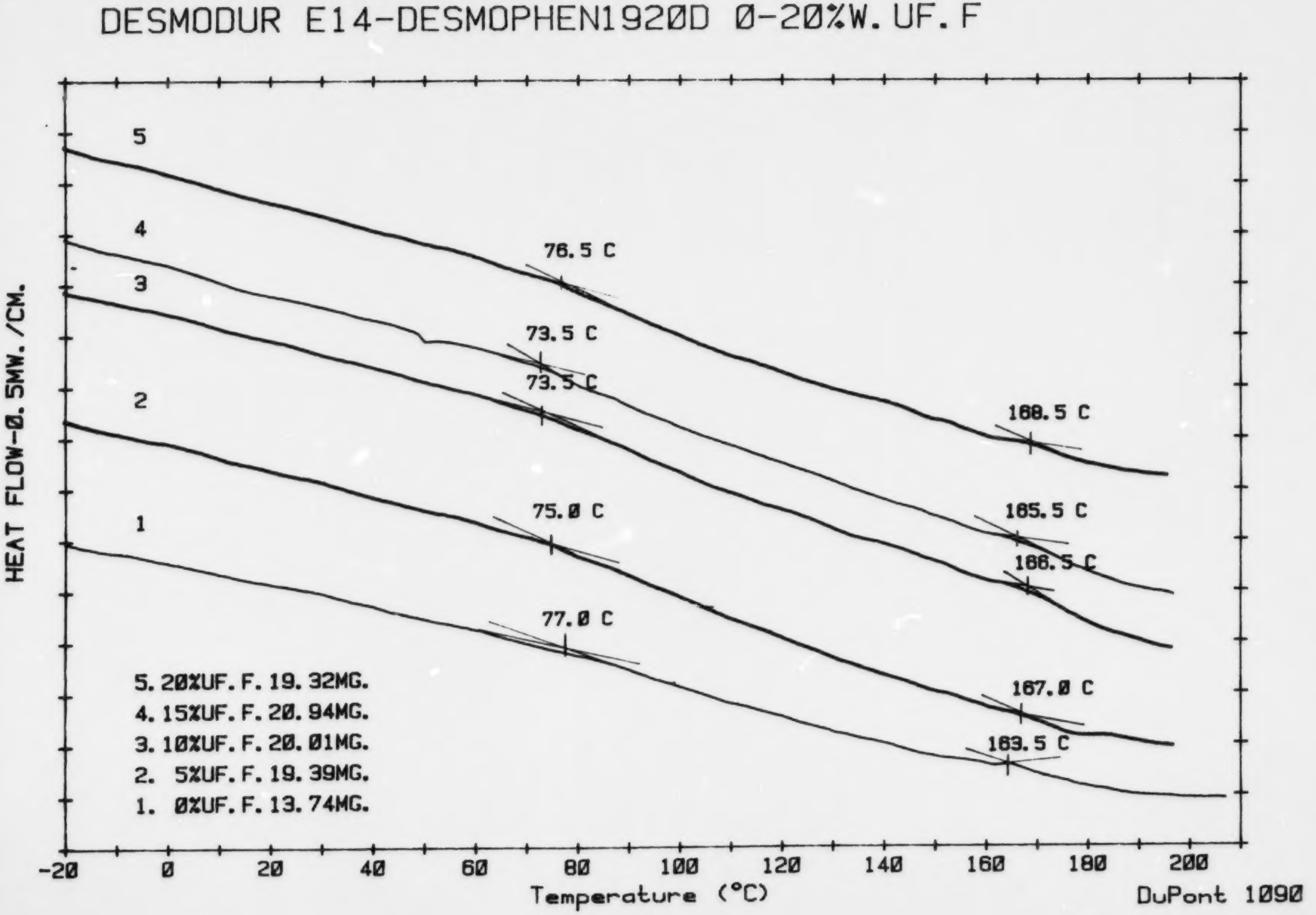


Figure 18 Extractibility of L from PU-L polyblends